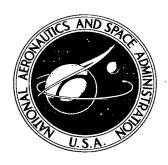
# NASA TECHNICAL TRANSLATION



NASA TT F-488

6.1



LOAN COPY: RETURN 10 AFWL (WLIL-2) KIRTLAND AFB, N MEX



# THE ORIGIN AND INITIAL DEVELOPMENT OF LIFE

by A. I. Oparin

"Meditsina" Publishing House, Moscow, 1966



### THE ORIGIN AND INITIAL DEVELOPMENT OF LIFE

By A. I. Oparin

Translation of "Vozniknoveniye i nachal'noye razvitiye zhizni." "Meditsina" Publishing House, Moscow, 1966.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

-					•
_		 	–		١

## TABLE OF CONTENTS

一門は世界後は、「上の中にはは、東京の中には、「中の一門」

	Page
Introduction	1
I. A Brief History of the Attempts to Solve the Origin of Life	7
II. Initial Stages in the Development of Carbon Compounds	32
III. Formation of the "Primary Broth"	56
IV. The Rise of Prebiological Systems	
11-	99
VI. Subsequent Evolution of Primary Organisms	119
Conclusion	146

#### THE ORIGIN AND INITIAL DEVELOPMENT OF LIFE

#### A. I. Oparin

ABSTRACT. This book presents a history of the development of life on Earth. It is established that our planet is about 5,000,000,000 years old, and fossils extending back to the Pre-Cambrian, or Proterozoic, era have been found in different parts of the globe.

がある。 
「一般のでは、 
「一般のできない。 
「一般のできない。 
「一般のできない。 
「一般のできない。」 
「一

call life.

This era was an immense stage in geological development, and began almost two billion years ago. It is usually divided into three geologopalaeontological systems: the Sinisian, beginning about 1200 million years ago; the Yenisei, beginning about 1500 million years ago; and the Sayan, beginning about 1900 million years ago. It is the author's opinion, however, that scientists still do not have factual data correctly determining the time that life began.

It is characteristic of the development of matter, however, that it has proceeded at a continuously accelerating rate. Abiogenic evolution of organic substances required billions of years. With the rise of life, the development went on much faster. Essential shifts in the evolutionary path of life occurred in the course of hundreds and tens of millions of years. The formation and biological development of man has taken only a million years. Social transformations have been accomplished in the course of millennia and centuries. When any new form of the motion of matter arises, the old forms are retained, but their role in further progress is negligibly small since their rates of development are several orders lower than the development rates of the new form of motion. occurred when old abiogenic methods of synthesis of organic substances dropped into the background, as compared to the faster biological syntheses.

It is the author's opinion that human progress is now taking place, not in the biological development of the individual, but through the advancement of his social life.

#### INTRODUCTION

When observing nature surrounding us, we can readily divide it into an inert, inorganic world, and a world of living substances. The world of living substances comprises an immense diversity of animals, plants, and microbes. Outwardly, they are all quite different, but we may immediately observe something which they all have in common, which distinguishes them from objects of the inorganic world and which compels us to include in one single concept — the concept of the "living substance" — dogs, trees, whales, insignificant insects or blades of grass, man, and the bacteria which may be distinguished under a microscope. All of them are characterized by something in common, which we

/5\*

<sup>\*</sup> Numbers in the margin indicate pagination in the original foreign text.

What is the essence of this "something"? What is the essence of life? It is impossible to formulate a rational outlook which correctly reflects objective reality without answering this question on a scientific basis.

In addition, this answer determines the practical activity of man in all of those areas where man deals with living substances — for example, in agriculture or in medicine. In all of these cases, the methods which man employs to influence living nature will be more fruitful, the more deeply he penetrates into the essence of life and correctly understands it.

History has taught us that throughout all of the conscious life of man, the /6 problem of the essence of life has been one of the basic spring boards for the bitter idealogical struggle between two irreconcilable philosophical camps — idealism and materialism. The leaders of the idealistic camp see the essence of life in a certain eternal, super-material origin which cannot be understood by experimental methods. This is the "psyche" of Plato, the "entelechy" of Aristotle, the undying soul or part of diety of different religious disciplines and beliefs, the Kantian "inner principle of action", the Hegelian "world mind", "living force" of the vitalists, the "dominating idea" of the neovitalists, and so on.

Matter, that objective reality into which we are constantly gaining a deeper insight by directly observing it and by studying it experimentally, is without life and is inert based on the idealists' position. It serves only as the material from which the soul or the mind creates living substances.

According to the concepts of idealism, in principle it is impossible to understand the essence of life by objectively studying nature which surrounds us on materialistic bases, since life itself is above matter and is spiritual; only by deep speculative self-understanding would it be possible to approach an understanding of that divine origin which we carry in ourselves. We can only passively contemplate the rest of the world of living substances, and based on these positions nothing can be said about a change or an alteration of living nature by man.

Materialism approaches the problem of the essence of life from a diametrically opposite point of view. Based on the facts obtained by science, materialism states that life, and all of the remaining world, is material in nature, and that we do not have to acknowledge any spiritual origin which cannot be understood experimentally in order to comprehend it. On the other hand, from the materialistic viewpoint, an objective study of nature surrounding us is a reliable method, which not only leads us toward an understanding of the essence of life itself, but also enables us to change and alter living nature in a certain direction for the benefit of mankind.

Extensive groups of biologists and naturalists consciously or spontaneously base their research on a materialistic understanding of living nature. Proceeding on this basis, their research is constantly enriching our scientific knowledge regarding life, enabling us to approach the essence of life. However, the essence of life can be understood in different ways within the limits of this materialistic concept of life.

Many scientists of the last century and many contemporary researchers, 17 based on a mechanistic concept of life, have assumed and continue to assume that, in general, an understanding of life consists only of explaining it to the fullest extent by means of physics and chemistry, and of the complete reduction of all living phenomena to physical and chemical processes. Based on these viewpoints, there are no specifically biological laws. Only laws governing inorganic nature really exist; these laws control all the phenomena occurring in living bodies. Thus, mechanism denies any qualitative difference between organisms and bodies of inorganic nature.

In contrast to this, dialectical materialism regards life as a special form of the motion of matter, which differs in qualitative terms from objects in the inorganic world. This form of the motion of matter is only characteristic of living substances.

According to dialectical materialism, matter is in constant motion; this motion is not something external to matter, but is rather related to its very essence. In this sense, the motion of matter cannot be regarded as only the displacement of material bodies in space; mechanistic displacement of this type represents only one (the lowest and the simplest) form of the motion of matter. Along with this, different objects of reality are characterized by other, more complex forms of motion which arise as new elements in the development of matter.

We may observe this development process everywhere in the world surrounding us. It is gradual in nature, and is directed toward the formation of higher and higher forms of the motion of matter. The new qualities of the material objects which are formed during the development process are absolutely real, but they did not exist before its formation in any latent form. They actually appeared anew only at the given development stage of matter, as more complex, diverse, and richer differentiated forms of motion.

Thus, when new elements appear, the previous forms of the motion of matter do not disappear. They are retained in the qualitatively new objects of reality, but they remain in the background. They are of very little value for the subsequent development of these objects, as compared with the value of new forms of motion. The future fate of qualitatively new natural bodies is primarily determined by their special properties and by new objective laws, which cannot be reduced by simple analysis to forms which were previously more primitive. In essence, this type of reduction is equivalent to denying genuine development, /8 and it distorts reality and is incompatible with the real dialectics of nature. This is exactly what the mechanists do with respect to understanding life. Completely ignoring the development of matter, they try to understand the essence of life on purely metaphysical terms. Roughly speaking, their method consists of breaking down the organism, like a clock, into individual screws and wheels. By studying these parts, they plan to understand the living substance as a whole.

There is no doubt that a detailed analysis of matter and the phenomena inherent to living bodies is extremely important and is absolutely necessary in order to reach a correct understanding of life. The outstanding advances in present-day biochemistry and biophysics represent a reliable proof of this. It is only possible to move rationally toward a scientific understanding of life by studying in detail the chemistry of the material substratum of life, by studying

individual substances and their composition, by studying individual reactions taking place in the exchange of matter as well as their relationships, and by understanding the bioenergetic, structural, and general physical properties of living things. To demonstrate the predominant role of physical and chemical research in this respect would be to force an open door. This role is undisputed, but the question is really whether this research is in itself sufficient for achieving the formulated goal, for understanding the essence of life. Apparently, it is not.

Regarding life as a qualitatively special form of the motion of matter, dialectical materialism formulates even the very problem of understanding life in a different way than does mechanism. For the mechanist, it consists of the most comprehensive reduction of living phenomena to physical and chemical processes. On the other hand, from the dialectical materialism point of view, the main point in understanding life is to establish its qualitative difference from other forms of the motion of matter. Life finds its clearest expression (as a special form of the motion of matter) in the specific interaction of living systems -- organisms -- with the environment surrounding it, in the dialectical unity of a living body, and in the conditions of its existence.

Biological metabolism lies at the basis of this unity. Within this unity, many tens -- and possibly hundreds -- of thousands of individual biochemical reactions are uniformly combined into a complex network  $^{(1)}$  of the conversion of matter and energy. The processes of synthesis and assimilation are closely related in this network. As a result of these processes, matter in the outer surroundings is converted into proteins and other compounds inherent in organisms. This network also includes the processes of dissimilation and decomposition which primarily serve as the source of energy which is necessary for life. As a result of this, any organism throughout its entire life is in continuous, internal motion, in a state of continuous decomposition and synthesis. Its apparent uniformity is only an outer expression of the exceptional efficiency with which the opposite branches of metabolism are coordinated. Due to this, a newly formed particle develops in the place of each disintegrated particle of protein or other substance. In this way, to a specific extent, the organism retains its constant form and chemical composition, without changing materially. One characteristic which distinguishes life qualitatively as a higher form of the motion of matter is the fact that in living bodies many biochemical reactions, which together comprise metabolism, are not only strictly inter-correlated in time and in space, are not only combined in a single order of continuous self-renewal, but this order is uniformly directed toward a constant selfpreservation and self-reproduction of the entire living system as a whole, which is exceptionally adapted to solving the problem of the organism existing under given conditions in the outer surroundings.

This complete adaptation or, as it is frequently called, "appropriateness" of the organization penetrates the entire living world from top to bottom, down to the very elementary forms of life. It is a requisite property of any living

The term "network" is used here and later on in the book, not in the spatial, but in the temporal sense, and refers to the interrelationship of the metabolic reactions.

body, but this adaptation is absent outside of this body, under the natural conditions of inorganic nature. It is a feature which is characteristic of life, which arises as something new during the process by which life is established. Therefore, inert, inorganic bodies do not have this "appropriateness", and it is futile to try to find an explanation of it only in the laws of the inorganic world, or only in the laws of physics and chemistry. In this "appropriateness", the idealists find the proof of the supernatural nature of life -the purposeful fulfillment by living beings of the plans of a higher spiritual source. It is natural that the mechanists base themselves on this -- the similarity of organisms to artificially produced mechanisms, machines. The construction, the inner organization of the machine -- the mechanists say -- always is designed to fulfill a certain specific operation, it is "appropriate". Outside of life, only in machines do we find this type of adaptation of the structure for functions to be performed. In addition, the operation of any machine may be readily reduced entirely to physical and chemical phenomena. On this basis, since Descartes up to the present day, men have strived to understand the organism as a very complex mechanism. In different ages, only the material formulation of this attempt has changed with the development of science and technology. Thus, in the XVII Century, living beings were compared with tower clocks, later with steam engines, and now with cybernetic machines which may fulfill several functions of the mental activity of man. Therefore, cybernetics is now frequently regarded as a new, universal method of understanding the very essence of life.

Naturally, this is not valid. Attempts to regard a living being as a mechanism have existed for many centuries. However, the more extensively we study the organization of living bodies, the more formal the analogy becomes between organisms and mechanisms. No matter what the organizational complexity and perfection of a modern electronic computer may be, in its very nature it is farther removed from man than, for example, the most primitive battery, although the latter does not have that differentiating nervous system which the machine imitates so successfully.

This difference between organisms and mechanisms is clearly apparent in their material nature, in the fact that living beings -- to use the expression of Engels -- are "albumin bodies", in the continuous nature of the metabolism or ganization, and in the nature of the energetics of living nature. It is particularly important to mention the fact that the analogy cited by the mechanists between organisms and machines cannot in any way explain what it is intended to explain -- the "appropriateness" of the organization of living beings. Machines are not simply inorganic systems operating on the basis of only physical and They represent the creation not of a biological, but of a higher chemical laws. social form of the motion of matter -- the social life of the people. "appropriateness" of the machine, the suitability of its structure for fulfilling specific works cannot be separated from the interaction of laws governing It represents the fruit of the psychic activity of man, the inorganic world. of his creative forces. Therefore, when the mechanists attempt to explain the inner suitability of organisms by an analogy with machines, they inevitably arrive at particularly idealistic conclusions -- at the understanding that the "appropriateness" of the human organisms is the result of the creative will of the creator, "the master of quantum mechanics", or, in simple terms, at a

<u>/11</u>

knowledge of the divine origin of life.

Thus, mechanism -- which is outwardly opposed to idealism -- arrives at the same deadlock as the latter in its attempts to understand the essence of life. This is due to the fact that it ignores metaphysically the dialectic course followed by the development of matter, and it attempts to understand life separately from its formation.

In rational terms, life can be understood materialistically only as a special form of the motion of matter, which arises in conformance with a law at a specific stage of the development of matter.

The great dialectician of ancient Greece, Heraclitus of Ephesus, and after him, Aristotle, taught that we can only understand the essence of things when we know their origin and development. These words which reverberate with deep meaning are absolutely valid with respect to understanding life.

Only by studying its course of development can we understand why those features which are characteristic of life were formulated, and not other ones, why new elements and biological laws which were previously absent arose during the process by which life was established, and why that organizational adaptability which surprises us in all living things was developed.

Therefore, contemporary naturalists are coming increasingly to the conclusion that the problem of the essence of life and the problem of its origin are inseparable, and are only two sides of the same coin. In addition, it is becoming increasingly apparent that we cannot (as was done until even recently) regard the formation of life as a sudden, isolated phenomenon, as a "lucky chance". It represents an inseparable component of the entire process by which the universe develops according to a law.

The development of our terrestrial life only represents an individual, separate branch of this general development. This branch is characterized by the fact that it is based upon the uniform development of carbon compounds and the complex systems produced from them.

The initial stages of this development are very universal, and are widely extended throughout space. They may be concentrated in very diverse celestial objects. However, subsequent stages in the development of carbon formations were characteristic for terrestrial conditions. They were directly related to the development of our planet.

The large amount of factual information which science has presently accumu- /12 lated enables us to trace our specific development on the Earth. This has opened the door wide for objective scientific research which attempts not only to explain in a speculative manner the greatest events of the past, but also to obtain experimental proof for the validity of this explanation. However, science cannot reach this position at once. Mankind must traverse a very long and tortuous path before it can find the correct road leading to a solution of the problem of the origin of life. The history of these attempts is very instructive, and we shall begin our discussion with this.

#### REFERENCES

- 1. Khollicher, V. Nature in the Scientific Picture of the World. Izdatel'stvo Inostrannoy Literatury (IL), p. 278, 1960.
- 2. Engels, F. Dialectics of Nature. Gospolitizdat, p. 44, 1955.
- 3. Oparin, A. Zhizn', yeye priroda, proiskhozhdeniye i razvitiye (Life, Its Nature, Origin, and Development). Izdatel'stvo AN SSSR, 1960.
- 4. Istoriya filosofii (History of Philosophy). Izdatel'stvo AN SSSR, Vol. 1, p. 464, 1940.
- 5. Descartes, R. Oeuvres philosophiques. Aimé et Marin. Paris, 1839.
- 6. Kocca, P. Cybernetics. IL, 1958.

- 7. Shrödinger, E. What is Life as Viewed From Physics? IL, p. 120, 1947.
- 8. Heraclitus of Ephesus. Fragments. Izdatel'stvo Muscaget, 1910.
- 9. Simplicius on Aristotle, De Caelo Ancilla to the Presocratic Philosophers. Oxford, 1952.

#### I. A BRIEF HISTORY OF THE ATTEMPTS TO SOLVE THE ORIGIN OF LIFE

For many centuries people believed that the Earth was flat and motionless /13 and that the Sun revolved about it, rising in the East and setting in the ocean or behind mountains in the West (Figure 1). This false conviction rested on direct uncritical observation of the phenomena of nature surrounding us. Observations of this sort have often inspired the thought that different creatures —as, for example, insects, worms, and sometimes even fish, birds, and mice — are not only born of their like, but are also directly generated of themselves, giving rise to themselves from mud, manure, earth, and other lifeless materials.

It is understandable what an immense significance these everyday uncritical observations had in forming the beliefs of ancient peoples, when nature was not yet studied in detail or subjected to analysis and calculation, but was perceived as a whole in direct contemplation by the senses (Ref. 1). In China, for example, it has been believed from the most ancient times that aphids and other insects are self-generated under the effect of heat and moisture (Ref. 2). The sacred books of India contain reports of the sudden genesis of various parasites, flies, and beetles from sweat and dung (Ref. 3). It may be read in Babylonian cuneiform writings that worms and other animals are formed from the mud of canals (Ref. 4).

In ancient Egypt the prevailing belief was that the layer of silt left by  $\frac{14}{14}$  the Nile at flood could generate living creatures when it was heated by the Sun. In this way, frogs, toads, snakes, and mice were formed. It was felt that this could be easily ascertained from the observation that their forward part is already finished and alive, while their rear part still represents unchanged moist earth (Ref. 5).

We find this tale also repeated among the ancient Greeks (e.g., in Diogenes of Apollonia) and in the works of the famous Roman scholar Pliny. It enjoyed wide dissemination in both East and West, both in the Middle Ages and later. No wonder that even in Shakespeare's tragedy Antony and Cleopatra Lepidus asserts that crocodiles in Egypt are bred from the ooze of the Nile by the warm southern

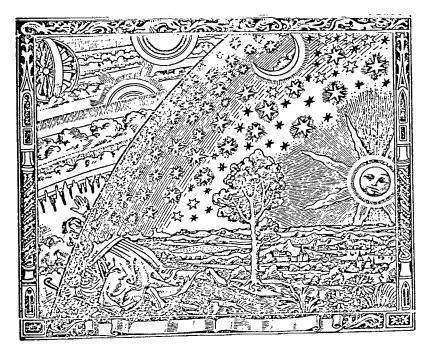


Figure 1. Picture of the World According to Medieval Concepts

sun (Ref. 6).

It is in general very characteristic of the problem in which we are interested that, among the most diverse peoples living at different times and on different stages of culture, we find reports of the spontaneous genesis /15 almost always of the same organisms -- worms generating in manure and decaying flesh, lice forming from human sweat, fireflies born of the sparks of bonfires, and, finally, frogs and mice originating from dew and humid ground. Everywhere that man encountered the sudden and large-scale appearance of living creatures, he regarded this as autogenesis of life. The belief in autogenesis among ancient peoples was, therefore, not a conclusion drawn from any particular conception of the world. For them, autogenesis of living creatures was simply an obvious, empirically established fact under which a certain theoretical foundation was subsequently laid.

Underlying the ancient teachings in India, Babylon, and Egypt of the origin of life were various religious legends and traditions. From this point of view, even the autogenesis of living creatures was only a particular case of the manifestation of the creative will of gods or demons. But already at the very sources of our European culture in ancient Greece, cosmogony, as the beginning of scientific investigation, comes to replace theogony, as the mythical interpretation of nature (Ref. 7).

Although all the Greek philosophers from the Milesians to Epicurus and the Stoics acknowledged autogenesis of living creatures as an indubitable fact,

their philosophical treatment of this "fact" already far exceeded the confines of previous mythical ideas. It contained in itself the germs of all the conceptions which were subsequently developed about the origin of life.

The most ancient philosopher of Greece, Thales, who lived around 624-547 B.C., was already approaching the problem of the essence and origin of life from spontaneously materialistic positions. The basic principle of Thales, like other philosophers of the Milesian school (Anaximander and Anaximenes), was the recognition of the objective existence of matter which is the eternally living, eternally changing elementary principle. Life is inherent in matter as such. Therefore, although the Milesians believed in the autogenesis of living creatures from mud. slime. etc., they treated this phenomenon merely as the self-formation of individual organisms which did not require the intervention of any special mystical forces to bring it about (Ref. 8). Later, the same idea was developed by Empedocles (485-425 B.C.), according to whom plants and animals may be formed from inorganic, but already living substances, or by birth from "their like" or from "things unlike them," i.e., by autogenesis (Ref. 9). However, a particularly clear expression of the idea of the self-formation of living creatures was found in the teaching of Democritus (460-370 B.C.) (Ref. 10). In this doctrine, ancient Greek materialism reached the culmination of its development, although it now assumed a rather mechanistic character. /16

The view of Democritus held that the basis of the universe is matter consisting of a multitude of very fine particles (atoms) in eternal motion and separated by empty spaces. This mechanical motion of atoms, which cannot be separated from matter, produces the formation of all individual things. In particular, life also is not a matter of divine creation, but the result of the mechanical forces of nature itself. According to Democritus, the primal generation of living creatures or their autogenesis from water and mud is the result of a random, but quite determinate, combination of atoms in their mechanical movement when the finest particles of the moist earth encounter and combine with the atoms of fire.

Epicurus (342-271 B.C.), another eminent thinker of ancient Greece, stood on the same philosophical grounds a hundred years later (Ref. 11). We find his views expounded in the famous poem by Lucretius Carus, On the Nature of Things (Ref. 12). According to this source, Epicurus taught that the moist heat of the sun and rain generated worms and numerous other animals from earth or dung. But this occurs without the participation of any spiritual principle. According to Epicurus, there is no soul as an immaterial force. The soul is material and consists of small, very fine, and smooth atoms. The mechanical combination of atoms in empty space also leads to the generation of multifarious things, in particular, of living beings. Here the principle of the motion of atoms is associated with matter, is based in matter itself, and does not depend on any "primary impetus" or other interference of the gods in the world's affairs.

Thus, already hundreds of years before our era many philosophical schools explained the phenomenon of autogenesis materialistically as a natural process of self-formation of living creatures without the participation of any spiritual forces. However, historically the situation evolved in such a way that the subsequent development of the idea of autogenesis did not become associated with

the materialistic "line of Democritus," but with the idealistic "line of Plato" inimical to it.

Plato himself (427-347 B.C.) hardly dealt with the problem of autogenesis. In the <u>Phaedo</u> alone does he cursorily pose the question of the possibility of generation of living creatures from the effect of heat and putrefaction. However, in complete agreement with his general philosophical principles, Plato asserted that plant and animal matter is not alive by itself, but may only be animated by the immortal soul, "psyche," which exists in it (Ref. 13).

This idea of Plato played an immense role in the subsequent development of /17 the subject in which we are interested. To a certain degree, it was reflected in Aristotle's doctrine which afterwards became the foundation of medievel scientific culture and dominated the minds of people for almost two thousand years. It was the opinion of Aristotle (384-322 B.C.) that, along with the birth of living creatures from their like, they have also always been selfgenerated from inert matter (Ref. 14). Thus, according to Aristotle, ordinary worms, the larvae of bees and wasps, as well as mites, glowworms, and various other insects are generated from dew, in the putrefaction of slime or dung, from dry wood, hairs, sweat, and flesh. All types of intestinal worms are generated by decaying parts of the body and excrementa. Mosquitoes, flies, moths, May flies, dung-beetles, cantharides, fleas, bedbugs, and lice (partly in this form, partly as larvae) are generated from the slime of wells, rivers, and seas, from the humus of fields, from mold, manure, from decaying wood and fruit, from animal impurities and dirt of every sort, from vinegar dregs, as well as from old fur (Ref. 15). Not only insects and worms, but also other living creatures may be autogenerated, says Aristotle. Thus, crabs and molluscs (Testaceans) are generated from moist earth and decaying muck; eels and some other fish, from sea-slime, sand and decaying algae. Even frogs, and under some circumstances also salamanders, could be formed of coagulated mud. Mice originate from damp earth. In the same fashion several higher creatures also originate which first arise in the form of worms. "Therefore for man and for quadrupeds," wrote Aristotle, "if they were at one time 'earth-born,' as some people assert, two methods of formation may be assumed -- either from a worm which is formed first, or from an egg." But in his works Aristotle did not only describe different cases of autogenesis. It is particularly important that he provided this phenomenon with a certain theoretical basis and created his own theory of autogenesis. In time his views apparently underwent a certain change, but in the last analysis they served as the basis for idealistic ideas of the origin of life.

Aristotle thought that living beings, like other concrete things ("essences"), are formed from the combination of some passive principle, "matter" (Aristotle evidently used this word to designate what we would now call 'material'), with the active principle, "form." For living beings, form is the "entelechy of the body," the soul. It forms the body and causes it to move. Therefore, matter has no life, but is encompassed by it, is teleologically formed, and is organized by the soul force, the goal-directed inner essence of which (the entelechy) /18 brings matter to life and keeps it alive.

Aristotle's views exerted tremendous influence on the entire subsequent

history of the question of the origin of life. With his incontestable authority, he confirmed the data of direct naive observations and for many centuries predetermined the subsequent fate of the doctrine of autogenesis. All the following philosophical schools, both Greek and Roman, shared Aristotle's opinion of the possibility of spontaneous generation of living creatures. Simultaneously the theoretical substantiation of this "phenomenon" in time took on a more and more idealistic, and even mystical, nature.

Certain works of the second and third centuries B.C. contain numerous tales and "marvelous stories" of the "pediculous misfortune" in which the juices of the human body changed into parasites, of the generation of worms and insects from decaying materials, crocodiles from the Nile slime, etc. Moreover, the philosophical school of the Stoics, the most authoritative of the time, taught that generation of animals and plants results from the action of the generative force belonging to the "pneuma."

From the late Stoics, this opinion was widely disseminated both in the Orient and the Occident by a number of philosophers and writers, in particular by Posidonius, who traveled extensively. This opinion had won general recognition in the beginning of the Christian era. In scientific treatises, political speeches, and artistic works of that time we continually come across descriptions of different cases of autogenesis. We find them in Cicero, in the famous geographer Strabo, in the universally educated Philo of Alexandria, in the historian Diodorus Siculus, and in such poets as Virgil and Ovid, and later Seneca, Pliny, Plutarch, and Apuleius (Ref. 16).

The doctrine of autogenesis was given a clearly marked idealistic character by the Neoplatonists (in the third century A.D.). Plotinus, the master of this philosophical school, taught that living creatures could be produced from the ground not only in the past, but could also be produced right now in the process of putrefaction. He explained this phenomenon as the result of the inspiration of matter by the "life-creating spirit" ("vivere facit"). Apparently, he was the first to formulate the concept of the "vital force," which has also come down to us in the doctrine of the modern vitalists (Ref. 17).

Early Christianity drew its guiding material on the autogenesis of life from the Bible, which in turn borrowed data on this subject from the mystic tales of Egypt and Babylon. The theological authorities of the end of the fourth and  $\frac{19}{19}$  the beginning of the fifth centuries, the "Fathers of the Christian Church," combined these tales with the doctrine of the Neoplatonists and on this basis developed their mystic conception of the origin of life.

Basil the Great, who lived in the fourth century, was and remains today one of the chief theological authorities of the Eastern Christian Church. It was under his influence that the leaders of orthodoxy formulated their ideas of living nature. His book <u>Hexaemeron</u> has remained in ecclesiastical literature, particularly in Russian, up to the present day. In this book we may read the following on the question of interest to us: "One creature is produced by the continuity of what has gone before; another even now is being born of the earth itself. For not only does the earth produce grasshoppers in rainy weather and thousands of other feathered breeds borne on the air — the majority of which, because of their smallness, do not even have a name — but it also sends forth

mice and toads. Near Thebes in Egypt when there is much rain during a hot spell, the whole countryside is suddenly filled with field mice. We find that eels are formed in no other way than from slime. They do not multiply from eggs or in any other manner, but derive their origin from the earth" (Ref. 18).

All these cases of autogenesis of living creatures\* occur, says Basil the Great, by divine command which continues to work with undiminished force from the creation of the world to our days.

St. Augustine is the same type of high authority for the Western Church as is Basil the Great for the Eastern. He also accepted the autogenesis of living creatures as absolute truth, and in his doctrine he strove only to substantiate this phenomenon from the viewpoint of the Christian Church. "Just as God," he wrote, "as a rule creates wine from water and earth by means of the vine and juice — but in some cases, as in Cana of Galilee, may create it directly from water — so in respect to living creatures he may cause them to be born of seed or to proceed from inert matter in which are laid 'spiritual seeds'" ("occulta semina") (Ref. 19).

In the autogenesis of living creatures, Augustine therefore saw the manifestation of divine arbitrary rule -- the animation of inert matter by the "vivifying spirit." He thus confirmed the doctrine of autogenesis as being entirely in conformity with the dogmas of the Christian Church.

Throughout the Middle Ages, the belief in spontaneous autogenesis held un- /20 interrupted sway over the minds of men. In the Middle Ages philosophical thinking could exist only as theological thinking under the cover of this or that doctrine of the Church. Any philosophical question could gain the rights of citizenship only on condition that it be connected with some theological problem. Philosophy was the "handmaiden of theology" ("ancilla theologiae"). The problems of natural science were shoved into the background. Surrounding nature was not judged from observation and experimentation, but from studying the Bible and theological works. Only very sparse information on mathematical, astronomical, and medical problems penetrated into Europe through the Arabs and Jewish scholars.

The works of Aristotle frequently reached the European peoples over the same route as very distorted translations. At first his doctrine seemed dangerous, but later -- when the church realized that this doctrine was entirely suited for many of its own purposes -- it raised Aristotle to the rank of "precursor of Christ in questions of natural science" ("praecursor Christi in rebus naturalibus"). Here, in V. I. Lenin's apt expression, "scholasticism and priestery took over the dead in Aristotle, but not the living ..."\*\* On the question of the origin of life, in particular, medieval theologians extensively developed the teaching of autogenesis whose essence they saw in the inspiration of lifeless matter by the "eternal divine spirit."

<sup>\*</sup> Many of these cases are obviously borrowed from Aristotle.

<sup>\*\*</sup> V. I. Lenin, Filosofskiye tetradi (Philosophical Notebooks). Marx-Engels-Lenin Institute (IMEL), Moscow, 1938, p. 332.

By way of an example, we may cite one of the most prominent leaders of scholastic Aristotelianism Dominican Albert von Bolshtedt, called Albert Magnus (1193-1280). According to legend, Albert Magnus was deeply occupied with zoology, botany, alchemy, and mineralogy. However, in his numerous writings he allots considerably less space to independent observations than he does to material borrowed from ancient authors. Concerning the problem of the origin of life, Albert completely adopted the theory of autogenesis. In his book "De mineralibus" he drew particular attention to the fact that the formation of living beings during putrefaction results from the "vivifying force" ("virtus vivificativa") of stars.

In his works on zoology, Albert Magnus gives numerous descriptions of the autogenesis of insects, worms, eels, mice, etc. from various types of rot-/21 ting materials, from the moist earth, vapors, sweat, and various unclean things. In just this way, the vapors of earth and water under the effect of heat and starlight engender numerous plants, not only mushrooms and sponges, but also roots, bushes, and trees, which often grow in places to which the seeds cannot be carried (Ref. 20).

St. Thomas Aquinas (1225-1274), the student of Albert Magnus, also adhered to the same opinion (Ref. 21). In his main work, the Summa Theologica, in questions on the origin of life he bases himself, on the one hand, on the views which he attributes to Aristotle, and, on the other hand, on the doctrine of Augustine of the "generating force" (anima vegetativa). Therefore, he fully admits the possibility of autogenesis in such animals as worms, frogs, and snakes in putrefaction, and the action of solar heat.

The teachings of St. Thomas Aquinas are to this very day acknowledged by the Roman Catholic Church as the only true philosophy. Therefore, the Western Church has carried through all the past centuries the principle which states that living beings are generated from lifeless matter by animation through a spiritual principle.

The theological authorities of the Eastern Church are also of the same In this respect, they base themselves principally on the dicta of Basil the Great. To illustrate this, we may cite here statements on the autogenesis of animals set forth considerably later -- in the eighteenth century -- by such outstanding figures in the Russian Church as Dimitriy Rostovskiy and Feofan Prokopovich. Dimitriy, Bishop of Rostov, who lived in the time of Peter I, in his work Brief Chronicle of Acts from the Beginning of the World to the Birth of Christ (Letopis', skazuyushchaya vkrattse deyaniya ot nachala mirobytiya do rozhdestva Khristova) (1708) wrote that Noah did not take animals capable of autogenesis into his ark. They perished during the flood and then were gener-"Those that are born of terrestrial moisture, of swamp and decay, ated anew. like mice, toads, scorpions, and other reptiles on the ground, and various worms, also beetles and cockchafers and locusts, and mosquitoes and midges and other such that are engendered by the dew of heaven -- all these perished in the flood and were born again after the deluge from the same substances" (Ref. 22).

Feofan Prokopovich (Ref. 23) in a course in theology which he gave in the Kiev Ecclesiastical Institute develops the same thought almost verbatim: "Let

us add that a multitude of animals which are engendered without the coupling of parents, but by themselves from putrefaction, did not need to be sheltered in the ark, like mice, worms, wasps, bees, flies, scorpions."

Even in the nineteenth century, the Archbishop of Nizhegorod, Benjamin, in the translation of a book by W. Frantsius (Ref. 24) pointed out that insects, worms, frogs, and mice are self-generated "from the rotting of logs, from the excrement of animals, from sea sand, from decayed earth, from corpses," etc.

/22

As we have already indicated, natural science in medieval Europe was on a very low level. It was in complete subjection to theology. The natural phenomena observed by travelers and scholars of that time were ordinarily not only discussed, but also were described as demanded by scholastic wisdom in complete conformity with the Scriptures and church dogmas. Therefore, the works of medieval scholars abound in the most fantastic descriptions and sometimes even drawings of the autogeneration of different insects, worms, and fish from slime and moist earth, of frogs from May dew, and even lions from desert rocks. Especially characteristic of medieval methods of understanding nature are the teachings, widely disseminated at that time, on the goose tree, the vegetable lamb, and the homunculus.

We find the tale of the goose tree as early as the beginning of the eleventh century in Cardinal Pietro Damiani (1007-1072). The English encyclopedist Alexander Neckam (1157-1217) develops the teaching of the formation of birds from the resin of conifers when they touch the salt of sea water. Subsequently this lore of the vegetable origin of geese and ducks became so accepted that their flesh came to be considered as fasting food, which was later forbidden by special order of Pope Innocent III. But, despite this, even at the end of the fifteenth century, i.e., almost three centuries later, the knight Leo von Rotsmital describes a dinner given in his honor in London by the Duke of Clarence in which ducks which spontaneously generated in the sea were served roasted under the name of fish, but Rotsmital' notes that the flesh of these "fish" tasted just like duck (Ref. 25).

The noted traveler Odorico di Pordenone (died 1331) was the first to mention the vegetable lamb. "Reliable" people told him that in the Tartar khanate of Khadli grow huge pumpkins which ripen and disclose lambs covered with white wool and having very tasty flesh (Ref. 26). Mandeville (1300-1372), describing his journey through Eastern countries, also tells of a whole tree in whose melon-like fruit live lambs were germinated. This tale passes from age to age and in the middle of the seventeenth century, was repeated anew by Adam Olearius in his descriptions of a journey to Muscovy and Persia. "They also told us," he wrote, "that there beyond Samara between the Volga and Don Rivers there grows a rare type of melon or, rather, squash which in size and kind resembles ordi- 123 nary melons, but whose exterior seems to resemble a lamb, having the very clearly outlined limbs of one, and the Russians therefore call it 'little ram'. This vegetable lamb feeds on the grass surrounding it, and is itself often the prey of wolves, which are very fond of it." Olearius writes further that he himself had the chance to see this "little ram" (Ref. 27).

The lore of the homunculus arose on the basis of alchemical experiments.

It apparently appeared as early as the first century of the Christian era. It was based on the idea that by mixing the passive maternal principle and the active masculine principle, the phenomena of generation may be artificially reproduced and the embryo of a little man -- the homunculus -- may be obtained.

Like the legend of the goose tree and the vegetable lamb, the tale of the homunculus also passes throughout all the Middle Ages and is encountered in a number of alchemical works, The typical representative of the early natural philosophy of the sixteenth century, Theophrastus von Hohenheim, who was known by the name of Paracelsus (1498-1541), in his works even gives a "precise formula" for making a homunculus.

Paracelsus was in general a convinced adherent of the autogeneration of living beings. He believed that the active vital force — the archeus — which may be controlled by the application of certain magic procedures, predominates in the bodies of animals and men. This force determines the formation of the organism and its subsequent development. In complete conformity with these philosophical views, Paracelsus amplified the idea of the spontaneous generation of life. He even adduced a number of observations which he made on the sudden appearance of mice, frogs, eels, and turtles from water, air, straw, rotting wood, and all sorts of waste products (Ref. 28).

In the second half of the Sixteenth, and particularly the geventeenth century, observations of the phenomena of nature were already becoming more accurate. Copernicus (1473-1543), Bruno (1548-1600), and Galileo (1564-1642) destroyed the old Ptolemaic system and formed correct ideas of the world of stars and planets surrounding us (Ref. 29). But this blossoming of precise knowledge still did not touch biological problems. The conception of primary spontaneous generation of living beings remained in full force in the minds of investigators of that period.

As an example, we may point to the noted Brussels physician van Helmont (1577-1644). He was already such a master of the methods of exact experimentation that he came close to solving the complex problem of plant nutrition, but at the same time he considered the possibility of spontaneous generation of living beings quite indisputable. Not only that, he substantiated this assump-  $\frac{1}{24}$ tion by a number of observations and experiments. A certain formula for producing mice from grains of wheat belongs to this very van Helmont. Since he thought that human exhalations could serve as the generative principle, it was necessary to put a dirty shirt into a vessel containing wheat seeds. In twenty-one days "fermentation" stops, and the exhalations of the shirt together with those of the grain would produce living mice. Here van Helmont was particularly struck by the fact that these mice which he produced artificially were just like the natural ones coming from the parental seed (Ref. 30). Harvey (1578-1657), who formulated the theory of the circulation of the blood, likewise failed to deny spontaneous self-generation. Although the famous phrase "Every living thing from an egg" (Omne vivum ex ovo) belongs to him, he gave the word "egg" here a very broad interpretation and considered spontaneous self-generation ("generatio aequivoca") of worms, insects, etc. completely possible as a result of particular forces manifesting themselves in putrefaction and similar processes (Ref. 31).

Harvey's contemporary and the father of English materialism of the seventeenth century, Francis Bacon (1561-1626), advanced the same concept. In his works he opined that various plants and animals (e.g., flies, ants, and frogs) may be spontaneously generated in the putrefaction of various materials. However, he approached this phenomenon from materialistic assumptions and saw in it only the proof that there is no impassable boundary between the inorganic and organic (Ref. 32).

The materialistic interpretation of autogenesis found especially clear expression in the teachings of Descartes (1596-1650) (Ref. 33).

Although this great French philosopher considered spontaneous generation of living creatures as beyond question, he categorically denied the thesis that this generation occurs under the effect of the "anima vegetativa" of the scholastics, the "archeus" of Paracelsus, the "spirit of life" of van Helmont, or of any other spiritual principle. In sharp conflict with the theological teachings and the anthropocentric tendencies of medieval physics prevailing at that time, Descartes attempted to reduce all of the qualitative variety of natural phenomena to matter and its motion.

Viewed in this way, according to Descartes, a living organism does not need any special law or "vital force" to explain it. It is nothing but a very complex machine whose structure is completely comprehensible and whose movements depend exclusively on the pressure and impact of particles of matter, like the movements of wheels in tower clocks. Therefore, different living creatures may /25 be self-generated from surrounding lifeless matter. In particular, when moist earth lies in the sunlight or when putrefaction appears, all types of plants and animals are generated, such as worms, flies, and other insects. The interference of a "spiritual principle" is not required for this. Autogenesis is only the natural process of self-formation of complex machines -- living creatures -- a process which always occurs under certain conditions which, to be sure, are as yet poorly studied.



Figure 2. Medal with Image of Francesco Redi.

Thus, until the middle of the seventeenth century, the very possibility of autogenesis of living beings was doubted by no one. The quarrel between the mystic teachings of the Middle Ages and rapidly developing materialism dealt only with the theoretical treatment of this phenomenon — whether to regard autogenesis as the manifestation of a "spiritual principle" or as the natural process of self-formation of living creatures.

The investigations of living nature, however, which were acquiring greater and greater scope and precision, began to shake confidence in the trustworthiness of the very "fact" of autogenesis.

The turning point in this respect is

rightly considered to be the experiments of the Tuscan physician Francesco Redi (1626-1698) (Figure 2). He had the honor of first coming forward with experimental refutations of the belief in autogenesis which has uninterruptedly prevailed for many centuries. In his work Experiments on the Generation of Insects (Esperienze intorno alla generazione degl'insetti) (1668), this scientist describes a number of his experiments which show that maggots in meat are nothing /26 but the larvae of flies. He put meat or fish in a large vessel covered with very fine Neapolitan muslin, and for still more reliable protection he covered the vessel with a framework on which muslin was stretched. Although many flies then lighted on the muslin, no maggots appeared in the meat itself. Redi pointed out that he had successfully observed how the flies laid their eggs on the muslin, but only if these eggs fell onto the meat did they develop into meat worms. Based on this, he came to the conclusion that putrescent substances are only the site or nest for the development of insects, but the necessary prerequisite for their appearance is the laying of eggs, without which worms are never generated.

It must not be thought that even Redi himself was completely successful in ridding himself of ideas about random autogenesis. Despite his brilliant experiments and correct interpretation of them, this scientist in other cases completely admitted the possibility of autogenesis, e.g., he thought that intestinal and wood worms were formed from decaying materials. In his opinion, the worms found in oak-galls were formed in just the same way from the plant juices.\*

This example graphically shows that a belief (although it is wrong) which has prevailed over the ages is not so easy to shake. Throughout the entire eighteenth century and even at the beginning of the nineteenth century, many scientists and philosophers of different specializations and schools -- and, even more, writers and poets -- frequently depicted in their works various fantastic cases of autogenesis of beasts, fish, insects, and worms, or noted the absolute possibility, from their point of view, of phenomena of this sort. Only very gradually, as the result of more precise observations of living nature and principally as the result of more detailed acquaintance with the structure of living creatures, was the impossibility of such complex formations being produced from structureless slime and decaying matter perceived. this way it became scientifically obsolete to believe in the random autogenesis of all highly organized living creatures. The idea itself of primary generation did not disappear. On the contrary, in the eighteenth and nineteenth centuries it was developed further in regard to the simplest and tiniest living creatures -- microorganisms.

After the Dutch scientist Anton van Leenwenhoeck (Ref. 35) (1632-1723), using magnifying glasses which he made with his own hands, discovered the new world of the tiniest living creatures invisible to the naked eye, these creatures began to be found everywhere where the putrefaction or fermentation of organic substances occurred. Microbes were found in different kinds of plant infusions and decoctions, in rotting meat, in spoiled broth, in sour milk, in

/27

<sup>\*</sup> Only later was this opinion refuted by the research of the Paduan physician and naturalist Vallisnieri (1661-1730).

fermenting wort, etc. A quickly spoiling or easily decaying substance had only to be set in a warm place for a short time and microscopic living creatures, which formerly were not there began immediately to develop in it. With the widespread belief at the time in autogenesis of living creatures, the opinion involuntarily appeared that precisely here, in the decomposing decoctions and infusions, autogenesis of living microbes from non-living matter was taking place. This idea was very authoritatively supported by the noted German philosopher Leibnitz (1646-1716) (Ref. 36) and the French naturalist G. Buffon (1707-1788) (Ref. 37).

The Scottish priest and naturalist John Turberville Needham (1713-1781) (Ref. 38) even set up special experiments with the aim of demonstrating the "autogenesis of microbes."

"I took a certain amount of very hot mutton gravy directly from the fire," wrote Needham, "and put it in a closed vessel with the cork fitted so tightly that it could be considered hermetically sealed." After this Needham again subjected the vessel to careful additional heating in hot ashes. But despite all this, after several days had passed the vessel was swarming with microorganisms. He made the same observations when studying different organic liquids and infusions. From this, he naturally drew the conclusion that autogenesis of microorganisms from decaying organic substances is absolutely possible, and even obligatory.

These observations of Needham's, however, were subjected to savage criticism by the Italian scientist Spallanzani (Ref. 39), who, like Needham, also conducted experiments aimed at establishing or refuting the possibility of autogenesis. On the basis of these experiments, he reached directly opposite conclusions. He asserted that Needham's experiments succeeded only because of insufficient heating of the vessels containing the liquid, and consequent incomplete sterilization thereof. He himself conducted hundreds of experiments in which plant decoctions and other organic liquids were subjected to more or less prolonged boiling, after which the vessel containing them was sealed, thus preventing access to the liquids by the air, which Spallanzani believed was the carrier of the microorganism germs. In all cases where this operation was conducted with reliable care, the liquids in the vessel did not putrefy and no living creatures appeared in them. Spallanzani was, nevertheless, unable to convince his contemporaries that he was right.

/28

The doctrine of autogenesis was defended even later by many naturalists and philosophers at the end of the eighteenth and beginning of the nineteenth centuries. It was developed, in particular, by the representatives of German idealistic natural philosophy. Although Immanuel Kant himself (1724-1804) (Ref. 40) believed that the primal internal origin of organisms lay in the supersensory (metaphysical) and that therefore the hypothesis of autogenesis was only a "bold adventure of the reason," the following natural philosophers -- Hegel (1770 -1831) (Ref. 41), Schelling (1775-1854) (Ref. 42), and Lorenz Oken (1779-1851) (Ref. 43) -- extensively developed the idea of autogenesis of life (generatio aequivoca) in their works. Along with these philosophical pronouncements, the first half of the nineteenth century also saw a series of experiments aimed at proving or refuting the possibility of autogenesis of

microbes. We must particularly note the experiments of T. Schwann (Ref. 44), F. Schulze (Ref. 45), H. Schröder, and T. Dusch (Ref. 46). Although they all primarily refuted the possibility of spontaneous autogenesis, they did not have sufficient proof.

In some cases, microorganisms appeared in the liquids for some reason. We now know that this happened because of some accidental technical error, but their contemporaries interpreted this differently. If desired, the appearance of microbes could easily be interpreted -- and in fact was interpreted -- as autogenesis which could occur in certain circumstances, although not always. These opinions were also held by such outstanding researchers as Dumas, Nägeli, and a number of other scientists of the mid-nineteenth century.

The conflict of opinions on the possibility of autogenesis of microorganisms reached its peak in 1859 when F. Pouchet (Ref. 47) published articles in which he described his experiments which seemed to show the possibility of autogenesis. Only about a hundred years separate us from Pouchet's experiments, but when we familiarize ourselves with these experiments we are involuntarily struck by their roughness and lack of cleanliness. However, Pouchet's work made a great impression on his contemporaries. The French Academy of Sciences put up a prize for the one who could throw light on the question of the primordial generation of living creatures by precise and conclusive experiments. The prize /29 was adjudicated to Louis Pasteur (1822-1895) (Ref. 48), who in 1862 published his work on random autogenesis, in which, by a series of brilliant experiments banishing all doubts, he proved the impossibility of microorganisms forming from various infusions and solutions of organic substances. Pasteur managed to do this only by departing from the beaten path of blind empiricism, by extensively covering the entire problem in his experiments, by giving a rational basis to all previous experiments, and by pointing out the sources of his predecessors' errors. He overthrew the previous idea that decaying infusions and decoctions give rise to microbes, and showed on the contrary that these liquids putrefy and ferment because of the vital activity of the microorganisms, whose germs were brought in from the outside. All attempts to overturn this thesis and discover cases of microbe autogenesis have proved to be in vain. From the modern point of view, this is quite understandable since microorganisms are not simple clumps of organic substance, as was thought before Pasteur. Detailed study of these primitive living creatures has shown that they possess a very complex and advanced organization. To now suppose that such a structure could be generated before our eyes from structureless solutions of organic materials is absolutely impossible. It is in essence just as absurd as to think that frogs are born of May dew or lions of desert stones.

Pasteur's research made an enormous impression on his contemporaries. And /30 that is understandable. The scientific feat performed by Pasteur may in essence be compared with that of Copernicus. In both cases, prejudices which had dominated the minds of men for thousands of years were overthrown. Nevertheless, these investigations did not represent a means of solving the problem of the origin of life. On the contrary, after them natural science was gripped by a profound crisis on this problem — a crisis which encompassed not only the end of the last century, but also almost the first half of our century. The cause of this crisis lay not in the nature of the problem itself (as the vitalists





Lazaro Spallanzani

Louis Pasteur

have tried to affirm) (Ref. 49), but in the methodologically defective mechanistic approach to understanding the very essence of life which prevailed in the natural science of this era.

The doctrine of mechanism has never acknowledged, nor does it now acknowledge, any fundamental qualitative difference between the inorganic world and that of living creatures. This makes an immediate and sudden transition from one world to the other — the autogenesis of living creatures — absolutely necessary. The simplest organisms must be generated from lifeless matter in the same manner as a crystal with a definite internal structure is formed from the structureless mother solution. Therefore, the primordial autogenesis of organisms is a logically necessary consequence of mechanistic views of life (Ref. 50). This is also the explanation of the insistent and very impassioned attempts experimentally to discover the autogenesis phenomenon which were made for a long time even after Pasteur's experiments (Ref. 51).

/31

All these attempts, however, came up against an absolutely impregnable wall of facts (Ref. 52). All reports of seemingly discovered cases of autogenesis proved false. They resulted from incorrect formulation of the experiment or wrong interpretation thereof, and were refuted when checked further. This knocked the ground out from under the feet of those researchers who saw in autogenesis the only way to solve the problem of the origin of life. Deprived of the possibility of experimenting in this direction, they fell into deep disillusionment and no longer endeavored to solve this "accursed" problem, but merely sought some substantiation of its insolubility.

Two opinions on this score had jelled by the beginning of our century. Some scientists, essentially maintaining the former positions of autogenesis,

considered this event not a happening governed by law, but the rarest "happy chance" which could, perhaps, occur only once throughout the existence of the Earth and therefore cannot be repeated in experimentation. Others, on the contrary, denied absolutely not only autogenesis, but even the origin of life in general. They tried to explain the appearance of our terrestrial life by germs introduced from other worlds which "may be regarded as everlasting storehouses of forms endowed with life, as eternal plantations of organic germs" (Ref. 53).

On this topic, H. Helmholtz wrote (Ref. 54), "It seems to me that if all our attempts to create organisms from lifeless material are unsuccessful, it is scientifically reasonable to ask ourselves the question, 'Did life indeed ever originate, or is it not as old as matter?'"

As early as the end of the last century, F. Engels (Ref. 55) subjected views of this sort to just and destructive criticism. He demonstrated that they confuse two completely different concepts: (1) the eternality of life as something which never occurred, but is only successively transmitted from one organism to another, and (2) constant, "eternal" genesis of life as a special form of motion in matter, and its creation anew whenever and wherever suitable conditions are formed for this.

We are now confident that our planet is not the only habitation of life, but that this form of the motion of matter has occurred and will occur in some other suitable objects in the universe. From this viewpoint, the arrival of living germs on Earth from other worlds, even if this were in fact discovered (which is very improbable), would contribute nothing toward solving the problem of the origin of life, since its genesis should in equal measure take place on Earth just as on other suitable celestial bodies.

Nevertheless, the search for such a possible arrival of germs extensively occupied the minds of scientists at the end of the last and the beginning of this century. Most frequently, hypotheses have been voiced that living germs were brought to Earth by meteorites or along with cosmic dust (the panspermia hypothesis). The first hypothesis was elaborated by H. Richter in 1865 (Ref. 56), and then supported by W. Thomson (Ref. 57), H. Helmholtz (Ref. 58), and P. Van Tieghem (Ref. 59), and others. According to this hypothesis, meteorites passing through the terrestrial atmosphere are strongly heated only on the surface, while on the inside they stay cold. Therefore, the germs of organisms said to live on the meteorites themselves, or on the planets from which they were formed, are preserved in them.

Numerous attempts to discover viable living germs, or at least their dead remains, directly in meteorites have yielded no positive results. S. Meunierre states (Ref. 60) that even Pasteur tried to isolate viable bacteria from a carbonaceous meteorite, but with negative results which he therefore did not publish. Much later, C. Lipman reported (Ref. 61) on microbes which he isolated from meteorites whose surfaces were sterilized and which were capable of multiplying on nutritive media. However, these microbes were absolutely similar to terrestrial ones and apparently were deposited as the meteorites fell to Earth. As recent model experiments by A. Imshenetskiy have shown (Ref. 62), this may easily happen by the formation in meteorites (carbonaceous chondrites) of deep cracks (sometimes reaching to the very center). As the meteorite falls to

Earth, these cracks suck in water and terrestrial contaminants (not only bacteria, but even the pollen of higher plants).

In our time (1962) Nady, Claus, and Hennessy have published a report (Ref. 63) stating that in the carbonaceous chondrites, Orgueil and Ivuna\* structured formations may be detected which, in the opinion of these authors, are the remains of organisms that once lived on the meteoritic material, but this opinion was not substantiated in further, more careful checking. As M. Briggs (Ref. 64) and E. Anders (Ref. 65) have demonstrated, the structured formations of Nagy et al. are mineral granules which are only similar to biological formations in appearance.

The second panspermia hypothesis was elaborated in detail at the beginning of this century by the famous Swedish physical chemist Arrhenius (Ref. 66). This scientist believed that living germs, together with particles of cosmic dust, may be transferred from one heavenly body to another under the pressure of light rays. Arrhenius calculated the speed at which this transfer must be effected and gave a number of reasons which he thought proved the possibility of the transfer of living germs through cosmic space in a viable condition. This latter assertion, however, has encountered very serious objections from subsequent researchers [P. Becquerel (Ref. 67), E. Grayevskiy (Ref. 68), and others]. Of particularly grave danger to the living germs are the shortwave ultraviolet rays permeating interplanetary and interstellar space which are fatal to everything alive. Modern space flights might give a direct answer to the existence of life beyond the confines of the Earth's atmosphere. However, as yet we have no positive data on this subject.

The penetration of man into space has engendered bold hypotheses stating that the primordial forms of life were perhaps brought to our planet at some time along with cosmonauts or astronauts, higher conscious beings, who made interplanetary and interstellar voyages. But hypotheses of this sort, which are widely disseminated chiefly in popular and science fiction literature, have as yet no factual foundation. It is interesting to note that our eminent scientist and remarkable inventor, K. Tsiolkovskiy (Ref. 69) -- in spite of his ardent faith in the possibility of interplanetary journeys -- categorically denied this sort of artificial introduction of microbes. In a 1919 manuscript left after his death, Origin and Development of Plants on the Earth, we read, "My work has shown that any living creature may be safely sent from Earth to another planet and be returned artificially by special procedures, but mankind will not be able to achieve this for a long period of time." But Tsiolkovskiy thought that such a transfer of life "with reason participating" had not occurred in the past, since we never have been able, and cannot now, discover traces of any higher living beings who have consciously journeyed across to us on Earth. "This," concludes Tsiolkovskiy, "means that life did not come to Earth from the planets, $\sqrt{34}$ even by way of the reason." Now, however, that the prospect of a flight to the Moon and the other closest planets is already becoming real, we must be careful not to infect these celestial bodies with terrestrial organisms, since this infection would greatly complicate the solution of the problem of the origin of life beyond the Earth's confines.

The adherents of autogenesis have, along with the assertion that this type of origin for primordial organisms was the rarest "happy chance," also developed \* Translator's Note: Tanganyika. Date of fall: 1938.

the idea that it required certain exceptional conditions, which existed at some past time on Earth but are now lost, for life to originate.

This idea was again particularly clearly formulated in the second half of the last century by an outstanding German naturalist of the time, E. Haeckel, who (Ref. 70) believed that the most primitive organisms must at some time have been spontaneously generated from inorganic matter as the result of the formative action of certain special external physical forces. This, Haeckel believed, was not in conflict with the fact that we do not at present observe autogenesis of microbes. The apparent reason for this is that now these forces are lacking in the nature which surrounds us, but that they once occurred on the surface of our planet.

Haeckel himself did not consider it possible to represent these forces in any detail, due to the state of knowledge in his time. However, succeeding scientists with the same viewpoint cited in their discussions electrical discharges and ultraviolet light and special forces of chemical affinity, and later even the corpuscular emissions of radioactive elements, as such forces. As we will see below, all these factors must indeed have played the important role of energy sources in the transformation of organic substances during their evolution on the primordial Earth, but in themselves they, as such, could not of course have provoked the autogenesis of organisms, any more in the remote past than they could today.

Therefore, all attempts to use these forces under laboratory conditions to reproduce the self-formation of organisms from lifeless materials naturally ended in complete failure. All experiments of this type to create "vivifying granules" [by R. Dubois (Ref. 71)], "cells" generated by radium [by M. Kuckuck (Ref. 72)], "plasmogenes" (Figure 3) [by A. Herrera (Ref. 73)], or artificial "fungi and algae" by S. Leduc (Ref. 74)] are extremely primitive and naive in  $\frac{35}{100}$  nature. Acquaintance with them makes it to a certain degree understandable, why in the biological literature of the 1920's and 1930's, an extremely negative attitude toward this problem became established, just as toward a problem whose solution is not worth the time of a serious investigator.

This was the hopeless blind alley into which the metaphysical approach to the problem of the origin of life led natural science. Quite different prospects for this problem opened up before scientists after employing the evolutional method of solution.

The significance of this method for the problem which interests us was first evaluated by Lamarck (Ref. 75). In his work, <u>An Analytic System of Positive Knowledge of Man</u> (1820), he regarded the origin of life from the inanimate as a process of gradual development of matter.

In the 1870's Engels (Ref. 55) pointed to the evolutionary development of matter as being conclusively the only possible method by which life originated. Life, according to Engels, does not exist forever nor does it suddenly generate spontaneously; it arises in the evolution of matter everywhere and at all times when the necessary conditions are created for this type of evolution.

This profoundly meaningful thesis of Engels' was not, however, sufficiently

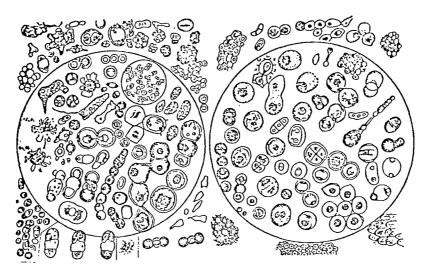


Figure 3. A. Herrera's Artificial "Cells"

widely reflected in the works of the naturalists of his time. Only very few of /36 them, and then only in general terms, declared the significance of the evolutionary principle for solving the problem of the origin of life. Here we may note the statement of the eminent Russian botanist and cytologist V. Belyayev in the University of Warsaw in 1893 (Ref. 76), and in particular the speech given by Sir. E. A. Schafer at the annual meeting of the British Federation in Dundee in 1912 (Ref. 77). Touching on the problem of the origin of life, Schafer said in this speech, "We not only have the right, but are even forced to believe that living matter in the past owed its origin to causes which, in nature, are analogous to those which have acted in the formation of all other forms of matter in the universe, in other words, to the process of gracual evolution .... Looking at the evolution of living matter from the standpoint of, and in the light of, evolution of matter in general, we become convinced that this living matter did not arise from a sudden transformation caused by a natural or supernatural force, but by a gradual modification process ...."

K. Timiryazev (Ref. 79) had a very high estimation of these statements by Schafer, and completely associated himself with the latter. But neither Shafer himself, nor any other of the scientists of the time could in any way specifically elaborate upon the course of the evolution which they declared. On the contrary, Schafer felt that this type of elaboration could not be achieved at the present level of knowledge.

The main obstacle which immediately appeared to block any attempts at specific representation of evolution as the progenitor of life was the conviction, which was common at that time, that organic substances could, and in fact always did, come into being only biogenically by the intermediation of organisms.

At the turn of the century, to be sure, the experiments of F. Wöhler (Ref. 79), A. Butleroff (Ref. 80), M. Berthelot (Ref. 81), and an entire galaxy of other chemists dealing with the artificial synthesis of organic substances were \* Translator's Note: Generally known in scientific circles as E.A. Sharpey-Schafer.

already well known, but this in no way shook the above convictions. It was considered that in this case these syntheses were also accomplished by a living being — by man, who consciously reproduces a specific sequence of chemical reactions which are lacking under natural conditions outside of living beings.

Moreover, all direct observations under natural conditions always consonantly and unambiguously revealed exclusively only the biogenic formation of organic substances on the Earth's surface. All people now living on our planet exist today only because of the organic substances whose formation has resulted from the vital activity of organisms, in the process of photosynthesis or chemosynthesis of green plants or of specific bacteria. Not only that, but the organic /37 fossil substances of petroleum and coal also primarily bear the biogenic stamp of their origin, since they are principally products of the profound disintegration and transformation of the remains, buried in the Earth's crust, of organisms which at one time existed upon it. Hence the conclusion was drawn that formation of organic substances under natural conditions is generally possible only by means of organisms (biogenically). Convictions of this sort naturally created seemingly unconquerable difficulties on the road toward solving the problem of the origin of life. Organic substances provide the basis of the material substrate of all living beings. Without them there is no life on our planet, since only the regular interaction of these substances can determine a certain dynamic organization of living bodies in time and can comprise the essence of the biological metabolism of materials. Therefore, it is understandable that a study of the evolution of matter, on the road toward the origin of life, must begin by solving the problem of how the most primitive representatives of organic compounds were formed in the beginning. But if these substances may be formed under natural conditions only in the vital activity of organisms, we involuntarily enter upon a vicious circle from which there seems to be no exit.

In my report given at the Russian Botanical Society in 1922 (Ref. 83), I endeavored to show that such a "desperate" situation is created only when we restrict our studies to the situation existing on the Earth in our era. If, however, we expand the circle of our investigations, proceed beyond the confines of our planet, and become acquainted with facts relative to other heavenly bodies, the result will be different.

Investigations of this sort show that in many varied objects in our stellar world, we may detect the simplest organic substances, which indubitably arose with no connection at all to life (abiogenically). This forces us to assume that our planet likewise was no absolute exception in this connection, and that the abiogenic formation of organic substances occurred when the Earth was still lifeless, and that only later, with the development of life, was this process overshadowed by more rapid and extensive biogenic syntheses.

The year 1924 saw the publication of my little book The Origin of Life (Proiskhozhdeniye zhizni) (Ref. 83). In it for the first time (of course, still very much in outline) I set forth the views which I gave in more elaborated form in subsequent editions (Ref. 84). In it I particularly attempted to demonstrate /38 the possibility of primordial abiogenic formation of the simplest organic substances — the hydrocarbons — on our planet. The evolution of these substances had to lead to the formation of protein—like compounds, and then to colloid systems capable of gradually improving their internal organization by the

operation of natural selection.

Somewhat later (1929), an article was published by J. B. S. Haldane (Ref. 85) which was very significant in the development of research on the origin of life. In this article the author also demonstrated that organic substances were generated before the formation of primordial organisms, and he also developed evolutionary views of this process.

The concept of the primitive formation of organic substances on Earth began to spread more and more widely in scientific circles, particularly after hydrocarbons were discovered to be present in the atmosphere of the large planets and their satellites, in interstellar gas-dust matter, and in other objects in space. This was greatly assisted by the work of a number of astronomers, physicists, chemists, and geologists. Here in particular, we should note the book by H. Urey, The Planets, Their Origin and Development (Ref. 86) and that by J. Bernal, The Physical Basis of Life (Ref. 87).

Solution of the problem of the subsequent evolution of primordial carbon compounds on our planet, and their transformations under the conditions of the Earth's ancient hydrosphere and atmosphere, was aided by numerous experiments reproducing these conditions in the laboratory. These experiments were successfully begun by the American scientist S. Miller (Ref. 88), who obtained amino acids — those most important components of the protein molecule — in the action of silent discharges into a gaseous mixture consisting of methane, ammonia, hydrogen, and water vapor. T. Pavlovskaya and A. Pasynskiy (Ref. 89) similarly synthesized amino acids under the influence of shortwave ultraviolet light.

Subsequently, investigations of this sort began to be performed by many scientists in several countries in the world. We will describe these studies in detail in the following discussion. Here it need only be noted that these experiments synthesized a large number of different substances — as well as their polymers which were similar to proteins, nucleic acids, etc. — from primitive carbon compounds. At the same time, extensive studies on the primary formation of multimolecular structures from these polymers, the occurrence in them of primitive metabolism, etc., were made.

In the middle of our century there has therefore occurred a decisive turn-/39 ing point in the attitude of naturalists toward the problem of the origin of life.

Previously, this problem -- if we may so express ourselves -- was under a ban, and there were very few works on it in scientific literature of the time, having in most cases only a general, speculative nature. In contrast to this, the number of studies in the last 10 to 15 years in the field in which we are interested has risen steeply, with the result that the need has even been created of uniting researchers in the different specialties and of correlating their work. A union of this sort was accomplished at the Moscow Symposium on the Problem of the Origin of Life, convened in 1957 by the Academy of Sciences USSR, on the initiative of the International Biochemical Union (Ref. 90).

This symposium played an important role in advancing us farther toward a solution of the problem of the origin of life. It not only summarized the

previous research, but also indicated ways to coordinate the work of scientists in different countries and specialties.

A worthy continuation of the Moscow Symposium was the Conference on the "Origin of Prebiological Systems," organized in the village of Wakulla Springs, Florida, in 1963 (Ref. 91). This conference showed that the problem of the origin of life had progressed beyond the stage of general speculative considerations. Its solution is now being effectuated on the basis of rigorously scientific observations and experiments. Moreover, it is no longer a question of hopeless attempts to discover sudden autogenesis of organisms, as was previously the case, but to study and experimentally reproduce completely possible phenomena, which are even necessarily specified by a law, occurring in the evolutionary development of matter.

To be sure, we are presently unable to detect the primitive origin of life in the natural conditions surrounding us, since the evolutionary process of carbon formations had an irreversible, unidirectional nature. We are also incapable of artificially reproducing this entire process as a whole in the form in which it arose in nature, since it spread over more than a billion years, but the separate stages in this process are quite accessible to objective scientific investigation. At present, the following three methods are being successfully employed for that purpose.

- 1. Discovery and study of the separate links in the evolutionary process under natural conditions, in the case where these conditions are right now the same as they were in the era before ours, i.e., before the development of life./40 This research method extends not only to our planet, but also to other objects in the universe, whose study is assuming for us more and more significance as man penetrates space.
- 2. Artificial reproduction in the laboratory of the conditions which prevailed on the still lifeless Earth at individual stages in the evolution of carbon compounds. The study of the processes occurring under these conditions (synthesis of more and more complex organic compounds and formation of multimolecular systems from them), and, finally, the formulation and study of models of these systems and processes.
- 3. Comparative biochemical investigations of modern organisms which are on different levels of development. These investigations make it possible to clarify the evolutionary order of metabolism and its earliest links occurring in the very process by which life was established. The data thus derived are those from which the formulation of artificial models, provided with progressively more complex metabolism, must start.

The advances already made at present on the road toward employing these methods foster the hope that the time is not distant when the simplest forms of life may be artificially reproduced by simulating in accelerated form the entire process by which life developed, and replacing protracted natural evolution by the conscious construction of systems and specific combination of processes which were at one time successive links in the evolutionary chain. But this first of all means that we must have at our disposal accurately established and experimentally verified data on the sequential course of evolution, in the form

in which it occurred under natural conditions on the surface of our planet.

#### REFERENCES

- 1. Lippman, E. Urzengung und Lebenskraft (Generation and Vitality). Springer, Berlin, 1933. Arbman. Arch. Religioswissenschaft, V. 29, p. 293-320, 1931.
- 2. Bodenheimer. Materialien zur Geschichte der Entomologie (Materials for the Study of Entomology). V. 1, 24, Berlin, 1928.
- Denssen. Geschichte der Philosophie (History of Philosophy). Leipzig, 1908.
- 4. Growther, I. Science Unfolds the Future. Müller LTD. London, 1955.
- 5. Brugsch. Religion und Mythologie der alten Agypter (Religion and Mythology of the Ancient Egyptians). Leipzig, 1891.
- 6. Shakespeare, W. Antony and Cleopatra. OGIZ, Moscow, 1944.
- 7. Istoriya filosofii (History of Philosophy), Vol. 1. Izdatel'stvo Akademii Nauk SSR, Moscow, 1957.
- 8. Makovel'skiy, A. Dosokratovskaya filosofiya (Pre-Socratic Philosophy), Vol. 1, Part 1. Tipografiya Universiteta, Kazan', 1918.
- Tanneri, P. Pervyye shagi drevnegrecheskoy nauki (The First Steps of Ancient Greek Science). Tipografiya V. Bezobrazova. St. Petersburg, 1902;
   Gomperts, T. The Greek Thinkers. Translated from the German. Izdatel'stvo D. Zhukovskogo. St. Petersburg, 1911.
- 10. Deborin, A. Kniga dlya chteniya po istorii filosofii (Book for Reading /41 on the History of Philosophy), Vol. 1, Izdatel'stvo "Novaya Moskva," 1924-1925; Fragments of Democritus and Illustrations of His Teaching. Translated from the Greek by A. Makovel'skiy. See "Materialisty Drevney Gretsii" (Materialists of Ancient Greece). Gospolitizdat, Moscow, 1955.
- 11. Writings and Fragments of Epicurus. Translated from the Greek by S. Sobolevskiy. See "Materialisty Drevney Gretsii" (Materialists of Ancient Greece). Gospolitizdat, Moscow, 1955.
- 12. Lucretius Carus. On the Nature of Things. Izdatel'stvo Akademii Nauk SSSR, Moscow-Leningrad, 1946.
- 13. Rodemer. Lehre von der Urzengung bei den Griechen und Römern (Doctrine of Generation Among the Greeks and Romans). Dissertation, Giessen, 1928.
- 14. Aristotle. On the Origin of Animals. Translation from the Greek by V. Karpov. Izdatel'stvo Akademii Nauk SSSR, Moscow-Leningrad, 1940.
- 15. Zeller, E. Die Philosophie der Griechen (Greek Philosophy). Reisland. Leipzig, 1923.
- 16. Apuleius. Metamorphoses. Translated by M. Kuz'min and S. Markish. Izdatel'-stvo Akademii Nauk SSSR, 1956.
- 17. Meyer, H. Geschichte der Lehre von den Keimkräften (History of the Doctrine of Germinal Forces). Haustein, Bonn, 1914.
- 18. Basil the Great. Hexaemeron. Svyato-Troitse Sergiyeva Lavra, 1902.
- 19. Quoted from E. Lippman, Urzengung and Lebenskraft (Generation and Vitality), Springer, Berlin, 1933.
- 20. Sighart, I. Albertus Magnus, sein Leben und seine Wissenschaft (Albertus Magnus, His Life and prience). Manz, Regensburg, 1857.
- 21. Shtekl', A. Istoriya sa nevekovoy filosofii (History of Medieval Philosophy). Izdatel'stvo Sablina, Moscow, 1912.
- 22. Dmitriy Rostovskiy (D. Tuntalo). Letopis', skazuyushchaya vkrattse deyaniya ot nachala mirobytiya do rozhdeniya Khristova, sobrannaya iz bozhestvennogo pisaniya i iz razlichnykh khronografov i istoriografov grecheskikh,

- slavyanskikh, rimskikh, pol'skikh, i inykh (Brief Chronicle of Acts from the Beginning of the World to the Birth of Christ Collected from Holy Scripture and from Various Greek, Slavonic, Roman, Polish, and Other Chronographers and Historiographers). Sochineniya (Works). Vol. 4, Moscow, 1857.
- 23. Prokopowicz, T. Christianae orthodoxae theologiae in Academia Kiowiensi (In the Kiev Academy of Orthodox Christian Theology), Vol. 1, Leipzig, 1782. See also Sobol', S. Istoriya microskopa i mikroskopicheskikh issledovaniy v Rossii v XVIII veke (History of the Microscope and Microscopic Studies in Russia in the Eighteenth Century). Izdatel'stvo Akademii Nauk SSSR. Moscow-Leningrad. 1949.
- 24. Frantsius, V. See B. Raykov. Zhurnal Ministerstva Narodnogo Prosveshceniya, No. 11, Section 3, 1916.
- 25. Quoted according to E. Lippman. Urzengung und Lebenskraft (Generation and Vitality). Springer, 1933.
- 26 Tschirch, A. Handbuch der Pharmakognosie (Manual of Pharmocognosy). Tauchnitz, Leipzig, 1909.
- 27. Olearius, Adam. Detailed Description of the Journey of the Holstein Embassy to Muscovy and Persia in 1633, 1636, and 1639. Translated from the German by P. Barsov. Tipografiya Universiteta, Moscow, 1870.
- 28. Darmstaedter, E. Acta Paracelsica (Acts of Paracelsus). München, 1931.
- 29. Gurev, G. Sistemymira (World Systems). Izdatel'stvo Akademii Nauk SSSR, Moscow-Leningrad, 1940.
- 30. Bulloch, W. History of Bacteriology. Oxford Univer. Press. London, 1938.
- 31. Meyer-Steinig, T., Zudgof, K. History of Medicine. Translated from the German. Gosizdat, Moscow, 1925.
- 32. Bacon, F. The Works of Francis Bacon, V. I., Reever. London, 1879.
- 33. Descartes, R. Oeuvres philosophiques (Philosophical Works) Aime et Martin. Paris, 1838.
- 34. Redi, F. Esperienze intorno alla generazione degl'insetti (Experiments on Insect Generation), 1668.
- 35. Leenwenhoeck, A. Arcana naturea detecta (Secrets of Nature Revealed).
  Delphis. Batavia, 1695. See also V. Omelyanskiy. Osnovy mikrobiologii
  (Foundations of Mikrobiology). Gosizdat, Petrograd, 1922.
- 36. Leibnitz, G. Monadology. Selected Philosophical Works. Translated from the German. Tipografiya Kushnareva. Moscow, 1908.
- 37. Nordenskiold, E. Die Geschichte der Biologie (History of Biology). Fischer. Jena. 1926.
- 38. Needham, T. Philosph. Trans. N. 490, p. 615, 1749; Idee sommaire ou vue generale du système physique et mètaphysique (Total Concept or General View of the Physical and Metaphysical System). Bruxelles, 1776; Bulloch, W. History of Bacteriology, p. 74. Oxford, Univer. Press. London, 1938.
- 39. Spallanzani, L. Saggio di osservazioni microscopiche concernenti il systema della generazione dei sig. di Needham e Buffon (Essay on Microscopic Observations Concerning the System of Generation of Messrs. Needham and Buffon); Opuscolidi fisica animalee Vegetabile (Minor Works Concerning Physics, Animals, and Plants). Modena, 1776.
- 40. Kant, I. Kritik der Urtheils Kraft (Critiqué of the Power of Judgment). Lagade and Friedrich. Berlin-Liban, 1790.
- 41. Hegel, G. Encyclopedia of Philosophical Sciences, Vol. 2. Philosophy of Nature. Institute Filosofii Kommunisticheskoy Akademii, Moscow, 1934.

29

/42

- Schelling, F. Zeitschrift für spekulative Physik, Gabler. Jena, 1800.
- 43. Oken, L. Zehrbuch der Naturphilosophie (Textbook of Natural Philosophy). Schulthess, Zürich, 1843.
- 44. Schwann, T. Ann. Phys. and Chem., 41, 184, 1837.
- Schulze, F. Ann. Phys. and Chem., 39, 487, 1836. 45.
- 46. Schröder, H., Dusch, T. Liebigs Annalen, 89, 232, 1854.
- Pouchet, F. Compt. Rend., 47, 979, 1858; 48, 148, 546, 1859; 57, 756, 47. 1863; Héterogénie ou traité de la génération spontanée basée sur de nouvelles expériences (Heterogeny or Treatise on Spontaneous Generation Based on New Experiments). Bailère. Paris, 1859.
- 48. Pasteur, L. Compt. Rend., 50, 303, 675, 849, 1860; 51, 348, 1860; 56, 734, 1863; Ann. Sci. Nat., 1861; 16, 5; Ann. Chim. Phys. Ser., 3, 64, 5, 1862; Etudes sur la biére (Studies on Beer). Gauthier-Villars. Paris, 1876.
- Driesch, H. Geschichte des Vitalismus (History of Vitalism). Barth, Leipzig, 1922.
- 50. Haeckel, E. Naturliche Schöptungsgeschichte (History of Natural Creation). Reimer, Berlin, 1875.
- Pisarev, D. Podvigi yevropeyskikh avtoritetov (Feats of European Authori-51. ties). Sochineniya (Works). Vol. 5. Izdatel'stvo F. Pavlenkova, St. Petersburg, 1909-1913.
- 52. Bastian, H. The Beginnings of Life. Macmillan. London, 1872. Timiryazev, K. Vitalizm i Nauka. Socheneniya. (Vitalism and Science. Works.) Vol. 5. Sel'khozgiz, Moscow, 1938.
- Wagner, M. Augsburger "Allgemeine Zeitung", Beiloge, Oct. 6, 7, 8, 1874.
- Helmholtz, H. Forward to: W. Thomson and P. Tait. Handbuch der theoretischen Physik (Manual of Theoretical Physics). Braunschweig, 1874.
- 55. Engels, F. Dialectics of Nature. Gospolitizdat, Moscow, 1955.
- Richter, H. Schmidt's Jhrb. ges. Med., 126, 243, 1865; 148, 57, 1870.
- 57. Thomson, W. (Lord W., Kelvin). Brit. Assoc. Reports, 41, 84, 1871.
- Helmholtz, H. Ueber die Entstehung des Planetensystems. Vorträge und 58. Reden. (On the Origin of the Planetary System. Lectures and Talks). Braunschweig, 1884.
- Van Tieghem, P. Traite de botanique (Treatise on Botany), V. I., Paris, 1891. 59.
- Meunierref, S. Becquerel, P. Astronomy. Bull. Soc. Astron. de France 60. 38, 393, 1924.
- Lipman, C. Am. Mus. Novit, 588, 1, 1932. 61.
- 62. Imshenetskiy, A. In the Collection: Problemy evolyutsionnoy i tekhnicheskoy biokhimii (Problems in Evolutionary and Technical Biochemistry). Izdatel'stvo "Nauka", p. 20, 1964.
- Nagy, B., Claus, G., Hennessy, D. Nature, 193, 1130, 1962; Nagy, B., 63. Meinschein, W., Hennessy, D. Annals N. Y. Acad. Sci., 180, 534, 1963.
- Briggs, M. Nature, 195, 1076, 1962. 64.
- 65. Anders, E. Enrice Fermi Institute Preprint, 61, 51, 1961; Titch, W., Anders, E. Annals N. Y. Acad. Sci., 180, 495, 1963.
- 66. Arrhenius, S. Formation of the Worlds. Translated from the German. Izdatel'stvo Mathesis, Odessa, 1912; The Universe. Translated from the Izdatel'stvo "Nauka", Moscow, 1912; Living Path of the Planets. Translated from the German. Izdatel'stvo Gosizdat, Moscow-Petrograd, 1923.
- 67.
- Becquerel, P. Comp. Rend., 151, 86, 1910. Grayevskiy, E. Doklady Akademii Nauk SSSR, 53, 849, 1946.
- Tsiolkovskiy, K. Sobraniye trudov (Collected Works). Izdatel'stvo "Nauka", 69. 1964.

- 70. Haeckel, E. Generalle Morphologie der Organismen (General Morphology of Organisms), V. 1, Reimer. Berlin, 1886.
- 71. Dubois, R. Compt. Rend. Soc. Biol., 56, 697, 1904.
- 72. Kuckuck, M. Lösung des Problems der Urzengung (Solution of the Problems /43 of Generation). Barth. Leipzig, 1907.
- 73. Herrera, A. Bull. du Labor. de plasmogénie. Mexico, 1, 49, 1934; 1, 63, 1934; 1, 71, 1935, Science, 96, 14, 1942.
- 74. Leduc, S. Les bases physiques de la vie (Physical Bases of Life). Paris, 1907; Théorie physicochimique de la vie (Physicochemical Theory of Life). Paris, 1910; Colloid Chemistry, 2, 59, N. Y., 1928.
- 75. Lamarck, J. Analysis of the Conscious Activity of Man. Translated from the French. St. Petersburg, 1899. See also A. Studitskiy. Uspekhi Sovremennoy Biologii, 39, 3, 1955.
- 76. Belyayev, V. O pervichnom zarozhdenii (On Primitive Generation). Izdatel'-stvo Varshavskogo Universiteta, Warsaw, 1893.
- 77. Schafer, E. A. Life, Its Nature, Origin, and Preservation. Translated from the English. Gosizdat, Moscow, 1924.
- 78. Timiryazev, K. From the Scientific Chronicle of the Year 1912. Sobrannyye sochineniya (Collected Works). Sel'khozizdat, 7, 447, Moscow, 1939.
- 79. Wohler, F. Ann. Phys. and Chem., 12, 253, 1828.
- 80. Butleroff, A. Compt. Rend., 53, 145, 1861; Liebigs Annalen, 120, 295, 1861.
- 81. G'yel't, E. History of Organic Chemistry from the Oldest Times to the Present. Translated from the German. Gosudarstvennoye Nauchno-Tekhnicheskoye Izdatel'stvo, Khar'kov-Kiev, 1937.
- 82. Oparin, A. Doklad na zasedanii Russkogo botanicheskogo obshchestva (Report at the Session of the Russian Botanical Society). 1922.
- 83. Oparin, A. Proiskhozhdeniye zhizni (The Origin of Life). Izdatel'stvo "Moskovskiy Rabochiy", Moscow, 1924.
- 84. Oparin, A. Vozniknoveniye zhizni na Zemle (Development of Life on Earth).
  Biomedgiz, 1936; 2nd ed., Akademii Nauk SSSR, 1941; 3rd ed., Izdatel'stvo
  Akademii Nauk SSSR, 1957.
- 85. Haldane, J. The Origin of Life, 1929. "The Inequality of Man", Chatto and Windus, London, 1932; "Science and Human Life", Harper and Brothers, N. Y. and London, 1933.
- 86. Urey, H. The Planets, Their Origin and Development. Yale Univ. Press, New Haven, 1952.
- 87. Bernal, J. The Physical Basis of Life. Routledge and Kegan Paul. Press. London, 1951.
- 88. Miller, S. Science, 117, 528, 1953.
- 89. Pavlovskaya, T., Pasynskiy, A. In the Collection: Vozniknoveniye zhizni na Zemle (Development of Life on Earth). Izdatel'stvo Akademii Nauk SSSR, 1959.
- 90. Transactions of the International Symposium, 19-24 August, 1957," Ibid.
- 91. Transactions of the Conference on the "Rise of Prebiological Systems" in Wakulla Springs, Florida, 1963. Academic Press, 1964. (Translated from the English, Izdatel'stvo "Mir," Moscow, 1966.)

#### II. INITIAL STAGES IN THE DEVELOPMENT OF CARBON COMPOUNDS

The findings of modern astronomy disclose the amazing interrelationship between the entire galactic system as a single whole. The evolution of the universe now appears to us as a unified process of evolution, in which each successive stage is indissolubly connected to the preceding and may be understood by studying this preceding stage. Not very long ago, when the subject of the origin of life was discussed it was assumed as a matter of course that planets like the Earth existed and had certain dimensions and a certain chemical composition. However, we now know that the existence not only of the Earth, but also of many of the elements needed in its formation had their own beginning, their own history of development, and may be understood only by knowing the entire developmental history of the stellar universe.

This sort of knowledge requires that the human mind penetrate unimaginable depths of time and study events from which we are separated by many billions of years. This became possible only after objective methods were found to establish geological and astronomical time in absolute units of measurement (in years, millions or billions of years).

First of all the phenomenon of spontaneous radiactive decay of heavy elements, always proceeding at a uniform rate regardless of any external conditions, was utilized as the standard needed for this.

The period of this decay is proportional to the number of the parental atoms. Therefore, the decay constant of a particular radioactive isotope may be expressed by the term "half-life" of the given isotope, i.e., the time during which any number of its atoms decays to half of its original value.

The periods of half-decay of the different isotopes vary to a great degree -- sometimes these periods are very short, but there are isotopes whose decay periods are measured in billions of years. Thus, for example, the half-decay period of uranium of atomic weight 238 in its conversion to the lead isotope having an atomic weight 206 is four and a half billion years. By determining the relative content of these isotopes in particular rocks, we can derive a rather accurate idea of the time interval which has passed since the formation of this rock from the moment it solidified or crystallized. In addition to the transition of uranium into lead, other isotopic transformations are extensively used to measure geological time -- such as, for example, the transition of thorium 232 into lead 208, of potassium 40 into argon 40, of rubidium into strontium, etc. (Ref. 1).

This method is now widely applied to determine the age of individual sectors of the Earth's crust. The oldest geological layers preserved in Karelia, the United States, India, and South Africa show that it has been about 3.5 billion years since the time they solidified. In particular, determination of the radioactive age of the oldest rocks of the Kola Peninsula gives a figure of 3.6 billion years (Ref. 2). Determinations of this sort still do not enable us, however, to obtain a clear idea of the age of our planet itself, since the Earth's crust which we examine must have undergone numerous changes and oft-repeated local meltings associated with the convection of matter and hence with

<u>/44</u>

/45

a change in the isotope ratio.

There is no doubt that the Earth as a planet must have been formed considerably earlier than the oldest layers of its crust, since a certain time interval was required for their final hardening (Ref. 3).

It is at present assumed that certain indications in this respect must be obtained by determining the radioactive age of meteorites which have fallen on the Earth. These bodies from space result from the shattering of colliding asteroids (Ref. 4). These asteroids are very small — several hundreds of kilometers in diameter — which excludes the possibility of gravitational heating in them and favors rapid emission of the heat of radioactive decay.

Asteroids must therefore have had a very simple thermal history in comparison to planets like the Earth.

They could not, as a rule, have been subjected to volcanic melting, nor could there have occurred internal convection of matter, silicate transfer, liberation of gases, etc. Moreover, the rapid solidification of the asteroid material apparently had taken place soon after separation of the planetary coagulations in the gas and dust nebulae which engendered the solar system. Therefore, the radioactive age of meteorites can now be equated with the age of planetary matter. Direct datings by the radioactive method have shown that many of the meteorites solidified four to 4.4 billion years ago (Ref. 5). However, the so-called lead method establishes the time elapsed since the principal consolidation of meteorite material at 4.6 billion years. C. Patterson (Ref. 6) assumes that the age of the Earth may also be determined by this method -- the thermal processes, displacement of rocks, and gas losses notwithstanding. It is interesting that this age is found by Patterson to be 4.55 billion years. i.e., it very closely matches the age determined by meteorite investigation. F. Whipple, to be sure, notes (Ref. 7) that the possibility is not excluded that the Earth and the bodies which generated the meteorites may have solidified somewhat earlier.

A detailed study of the content in meteoritic matter of individual characteristic isotopes provides a basis for believing that the formation of the Sun and planets in the gas and dust nebulae which bred them involved some process which led to the formation of the heaviest elements, including radioactive ones.

The fact is that a study of uranium isotopes as early as the 1920's permitted E. Rutherford (Ref. 8) to make an attempt at determining the time of formation of these elements. Rutherford's research, and in our time that of W. Fowler (Ref. 9), V. Baranov (Ref. 10), and a number of other authors demonstrated that radioactive, and consequently all heavy elements included in the composition of the Earth and other planets of the solar system themselves, were formed no earlier than some 5-5.5 billion years ago.

This was confirmed in the work of E. Anders (Ref. 11), I. Reynolds (Ref. 12), and others with radioisotopes which have a shorter half-life, e.g., iodine-129 (half-life 12.7 million years). These works made it possible to determine the time interval between the formation of these isotopes and the

formation of the Earth. It proved to be small and lay between one or several \(\frac{147}{47}\) hundred million years. Consequently, the age of the heavy elements without which the formation of planets like the Earth is inconceivable does not far exceed the age of our planetary system, which was formed soon after these elements appeared in cosmic space. Their formation, however, does not represent the limit of those depths of time we can now determine. It may now be assumed that the process of stellar formation is continuously going on in our galactic system (Ref. 13). It is somewhat tentatively assumed that our galaxy consists of five different types of stellar population differing from each other in chemical composition, distribution of matter, internal motion, and absolute age (Figure 4).



Figure 4. Nebula of Andromeda -- A Star Cluster Resembling Our Galaxy

To the first, most ancient type belong the stars whose age is near that of our galaxy as a whole. Based on a number of data the age of our galaxy has recently been found by W. Fowler (Ref. 14) and F. Hoyle (Ref. 15) to be from 12 to 20 billion years. The oldest stars of our galaxy are members chiefly /48 of its central regions and comprise globular clusters. The greatest number of younger stars belongs to the disk system of the galaxy. Among them is our Sun in particular, which belongs among the stars of the third generation. R. Brownlee and A. Cox after making a detailed computation of the evolutional development of our luminary (Ref. 16), find its age to be in the vicinity of five billion years (i.e., within the time when our galaxy had already long been formed). The Sun's age therefore is somewhat greater than that of the Earth or of meteorites found by the radioactive method. Our galaxy also contains even younger stellar populations, including, in particular, the stars located in the immediate vicinity of the spiral arms of the galaxy.

The results given by a comparison of the old and relatively young stellar generations are very interesting. The stars of the globular clusters — these most ancient objects in the galaxy — have a far greater content of hydrogen as compared to metals than is the case in the younger stars, although it would seem that the longer a star had existed, the greater should be the "combustion" of hydrogen in it. This graphically demonstrates that the primordial medium from which stars of the first generation were formed consisted almost exclusively of hydrogen, but the stars of later generations — including our Sun in particular — were on the other hand formed from a mixture of light and heavy elements. Consequently, the latter were formed in the galaxy after its first stellar population had been originated.

Without the participation of heavy elements, however, planets of the terrestrial type could not have arisen.

Bodies of sufficiently large mass -- like stars -- can be formed solely of light elements, even almost entirely of pure hydrogen. This in all probability was also the case at the very beginning of the galactic system. Such a mass is quite stable, and with sufficient densification very simple thermonuclear reactions are developed which involve the transformation of hydrogen into helium and which serve as a source of stellar energy. But the existence of bodies of the size of our Earth formed of pure hydrogen is quite inconceivable, since the mass of these bodies is not great enough to keep hydrogen from dissipating in cosmic space. Hence, it may be concluded that in the first billions of years that our galaxy existed, when a sufficient amount of heavy elements had not yet managed to form, planetary systems like our modern one could not have existed, and therefore neither could life (originating as these planets evolved) have The conclusion must then be drawn that distribution of life in the universe is restricted merely to stellar populations of late enough types that they had at their disposal all the elements of the periodic system. In studying the cosmic history of the origin of life, we must therefore first of all form a concept of when and how these elements could form in our galaxy (Ref. 17).

This question still cannot be so easily answered. In 1959 a special International Symposium was devoted to it in Liege, where O. Struve (Ref. 18) and A. Cameron (Ref. 19) gave summaries of the modern state of knowledge on the chemical evolution of stars. Cameron indicated possible processes of element formation (nucleosynthesis): one was stable and involved the mechanism of stellar radiation in stable stars, and the other was unstable and involved the flares of supernovae.

The nucleosynthesis of light elements is exoergic in nature. The liberated energy resulting from it also provides the stellar radiation. Since electrostatic repulsion when hydrogen nuclei combine is relatively slight, the transformation of hydrogen into helium may proceed at temperatures of "only" a million degrees. It is possible in a contracting gaseous sphere consisting of hydrogen alone, and may begin after this sphere reaches the indicated temperature because of compression and the liberation of gravitational energy. In contrast to this, a temperature on the order of several billion degrees is needed to generate the heaviest elements and the radioactive elements. Such a temperature is not found in the interior of stable stars, but occurs only in the flares of supernovae.

Therefore, the radiation of stable stars comprising the main sequence of the Hertzsprung-Russell diagram (Figure 5) is maintained by the simplest nuclear reactions of transformation of hydrogen into helium, first by way of deuterium, and then with carbon as a catalyst. Subsequently, as the hydrogen is burned up, the star travels down the main sequence curve and is rather rapidly transformed into a red giant. Heavier elements can now be formed from helium together with carbon in its nucleus (Ref. 20). The formation of these elements is, however, limited here only to comparatively moderate series of numbers, chiefly up to neon-20 or magnesium-22, but neither can they be ejected by the star into surrounding space.

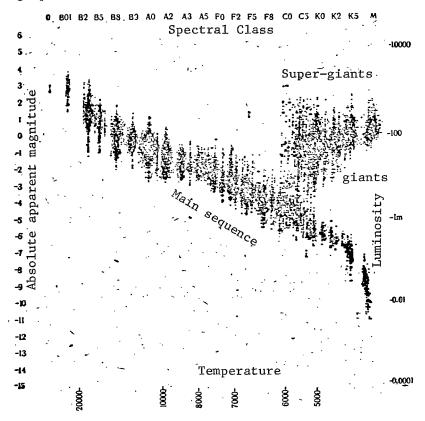


Figure 5. Distribution of Stars of Different Spectral Classes in the Hertzsprung-Russell Diagram

Cameron therefore believes that formation of all elements of the periodic /50 system (including the heavy radioactive elements) is possible only in the flares of supernovae. These catastrophic stellar explosions occur in our galaxy about every three hundred years. They are associated with the evolution of "billion-degree" temperatures and tremendous, although short-lived, pressures. In this process, an enormous amount of energy is liberated, and there is a gigantic ejection of matter outwards, in which the star loses a mass comparable to that of the Sun in a short time. The relatively light elements in the stellar material rapidly

increase their atomic weight by capturing the neutrons ripped from the stellar /51 nucleus. In this way the heaviest elements of the periodic system are generated. Part of the stellar matter is scattered in all directions by shock waves, and enriches the surrounding space with the heavy elements thus formed.

V. Fesenkov develops this thesis (Ref. 21), and on the basis of profound research into the isotopic composition of meteoritic matter arrives at the conviction that the Sun and the planets surrounding it were formed in a single process associated with the flare of a supernova in this region of the galaxy. This flare occurred about five billion years ago. It provided the solar system which was being formed with heavy elements, enriching it in this respect as compared with the stars formed before the Sun. At the same time, the supernova flare was attended by far-spreading shock waves which were able to compress the interstellar matter in a protosolar gas-dust cloud, disturb its gravitationally unstable state, and serve as an impetus to the subsequent formation of the Sun and planets. Similar supernova flares must have repeatedly happened in our galaxy both before and after the solar system arose. To illustrate the consequences of such events, Fesenkov points out the region of the constellation Cygnus which is occupied by an entire system of filamentary nebulae (Figure 6). Studies of different photographs of this region, made at an interval of half a century, showed that these filaments are dispersing at a considerable velocity from some common center which proves to be a source of radio-emissions. Fesenkov interprets this sort of phenomenon as proof of the explosion of a supernova at this point in the galaxy in the past.

The Mountain Astrophysical Observatory of the Astrophysical Institute of the Academy of Sciences of the Kazakh SSR also discovered a small number of star chains among these filamentary nebulae. These chains are unstable, recently-generated formations, each consisting of stars resembling each other in size and color and occurring at the same stage of evolution. "In a comparatively short time," writes Fesenkov, "these unstable star chains will cease to exist as such. The stars composing them will disperse, they will lose all connection with each other, and will travel independent, but similar, evolutionary paths." Fesenkov therefore associates the origin of the solar system with the burst of a supernova shortly before the formation of this system.

This supernova caused local condensations (extending to the formation of stars) in the surrounding gas-dust medium, and simultaneously determined the nucleosynthesis of heavy elements needed for planets of the terrestrial type.

D. Frank-Kamenetskiy visualizes (Ref. 22) the nuclear transformations occurring during the formation of our solar system in a different way. This author has now for a number of years been pointing out the possible significance of "cold" processes for the formation of elements. In this case, the nuclear particles receive the energy they need for nucleosynthesis not from heating (which requires "multimillion" and "billion-degree" temperatures), but from direct acceleration in the shock waves and magnetic fields.

During the genesis of the solar system, our Sun was in a stage of gravitational condensation, in its stage of condensation from a gas-dust cloud. It was still a very young star and, Frank-Kamenetskiy believes, at that time it might have been grouped with the observed and now young stars of the T Taurus



'igure 6. System of Filamentary Nebulae in the Region of Cygnus

type. These stars are in a state of violent activity. Their spectra reveal a peculiar non-thermal radiation -- direct evidence that the electrons here get their energy not from heating, but from certain "cold" processes. This indicates the possibility of the same sort of acceleration for nuclear particles. Therefore, the violent motions in the young star plasma, causing shock waves and variable magnetic fields to form, here create conditions for the "cold" synthesis of elements.

Comparing data derived from a study of the isotope content of a number of elements (particularly lithium, beryllium, and boron) in the Earth's crust, meteorites, the Sun, and young stars, Frank-Kamenetskiy arrives at the conclusion that planetary systems are born just when the star is passing through the T Taurus stage of its evolution. "When observing the violent, moving phenomena of non-thermal luminosity in these stars," he writes, "we are seeing the 'birth pains' of a planetary system being brought to light."

However that may be, we may assume that our planetary system was formed from protoplanetary material which includes all the elements of the periodic system and which originated shortly before, or even contemporaneously with, the formation of the planetary system itself. Later, only certain changes in isotope composition under the effect of cosmic rays could occur in it, but their significance is not at all comparable with those processes of element formation described above.

system, was formed from the material of a discoid gas-dust cloud which at one time surrounded our luminary (Ref. 23). This cloud was perhaps captured from cosmic space by the Sun (Ref. 24), but it is most probable that it was a remnant of the gas-dust nebula from which the Sun itself was formed (Ref. 25). In any case, the chemical composition of the material comprising it may be compared with the composition of present-day clusters of interstellar gas-dust matter. Here the gas is chiefly represented by hydrogen, which is the predominating element in space. Helium and other inert gases are present in smaller quantities. The remaining elements, the heavy metals in particular, comprise only hundredths, thousandths, and smaller fractions of one percent of the total cluster mass. The total composition of the present-day Sun, which includes by far the major part of the mass in the whole solar system, is also in direct conformity with a composition of this type.

Hydrogen makes up about 60%, helium 30%, carbon, nitrogen, and oxygen 1 to 2%, and the heavy elements together comprise less than 1% (Ref. 26).

H. Brown believes (Ref. 27) that all the substances comprising the original gas-dust solar nebula may be divided into the following three groups: the so-called gaseous group containing hydrogen, helium, and the noble gases, which keep their gaseous state at temperatures close to absolute zero. In the very low temperature prevailing in the original nebula, they were the chief constituents of its gas component. Further, the "ice" group is distinguished, containing substances formed from carbon, nitrogen, and oxygen (plus hydrogen), such as ammonia, methane, and water. Finally, the conventionally-termed "Earth" group is made up of silicon, magnesium, iron, etc. Their melting point is very high. Table I gives the relationships between these groups for the Sun (Ref. 28).

When, however, the planets were formed from the discoid protoplanetary cloud, these substances were greatly redistributed, as is evident from Table 2, which gives the present-day relationships between these groups for the different planets of the solar system.

We can for the time being only surmise the reasons for and the routes by which this redistribution of materials resulted while the individual planets

Т	٨	R	Т	¥	т
J.	м	.ID	ш	1.	

Groups	Earth —	Ice	Gas
Elements	Si, Mg, Fe etc. (plus 0)	C, N, O (plus H)	H, He
Relative mass	I	47	300—600
Melting point	2000°K	< 273°K	< 14°K

TABLE 2

Groups Planets	Earth	Ice	Gas
Planets like the Earth	1,00	<0,01	0
Jupiter	<0,01	1,0	0,9
Saturn	0,01	0,3	0,7
Uranus	0,1	0,8	0,1
Neptune	0,2	0,7	0,1
Comets	0,15	0,85	0

were being formed.

At present the cosmogonical literature contains many hypotheses for the mechanism by which the solar system was formed (Ref. 29). Both the vortical motions in the gasdust medium and gravitational forces are advanced for this, /55 while recently magnetohydrodynamic phenomena have been cited, in particular (Ref. 30). The majority of modern cosmogonists, proceeding from general physical laws, employ appropriate mathematical calculations to give a rational foundation to the manner in which those structural features possessed by our solar system today originated -- the laws governing the motion of the planets and their satellites, the shape of their orbits, planetary distances, size and mass of the planets, distribution of momentum between Sun and planets, etc. However, scarcely any of the presently existing hypotheses can fully satisfy all the demands made /56 upon it.

F. Whipple in his report (Ref. 7), recently presented at a meeting devoted to the centenary of the Washington

Academy of Sciences, assumes that a cloud of gas-dust matter which was part of the gigantic interstellar clusters was the original structure leading to the formation of the solar system. This cloud was of a size commensurate with the present solar system, of a low temperature of the order of 50°K (about -220°C), and a weak magnetic field, and contained approximately 1000 hydrogen atoms per cubic centimeter, as well as a considerable amount of dust. It was gravitationally unstable, having a certain turbulence and central condensation; in the final analysis this led to its general destruction. In this process — when the mass of the central body grew swiftly, rapidly becoming denser and being heated by gravitational energy, and later also by the hydrogen-helium reaction — it was transformed into our luminary. The remaining matter which was not included in the composition of the Sun was formed into a discoidal cloud which provided a beginning for the formation of "protoplanets."

40

In this protoplanetary cloud the process of gradual unification of the dispersed matter, first into relatively fine bodies, and then into coarser structures, incluctably had to occur. The cloud temperature, on the one hand, depended greatly on solar radiation and, on the other, on loss of heat by the cloud through radiation into interstellar space. Therefore, its temperature differed greatly on the periphery and in the central portions of the gas-dust disk. It was this situation which was to determine the distribution of protoplanetary material in the disk.

Closer to the periphery where intensive cooling took place, the substances of the "ice" group condensed at a high velocity, "froze" onto the "earth" particles, and formed so-called Cometesimals. Near the orbit of Jupiter and Saturn, the gas, dust, and cometesimals combined rapidly into large planets, which was assisted by the Sun's magnetic lines of force. Farther, toward the periphery, the cometesimals collected into the planets Uranus and Neptune, which are formed principally of cometesimal material. Consequently, part of this material went into the composition of Jupiter and Saturn, part formed Uranus and Neptune, and part fell into the Sun, or began to rotate around it in exceptionally elongated orbits and turned into comets. Finally, a certain amount of cometesimal matter was entirely lost to our planetary system by escaping into interstellar space.

The processes of planetary formation in the regions of the discoid cloud nearer the Sun, in the area where planets of the terrestrial type formed, must have developed in a different manner (Ref. 31).

<u>/57</u>

Here the gaseous component of the cloud was almost entirely lost, the "ice" was only partially retained, and the basic material was that of the "Earth" group. The clustering of dust particles consisting of this material led to the formation of so-called planetesimals — tiny bodies including in themselves all non-volatile substances of the primordial dust cloud — silicates and their hydrates, metals (particularly iron), their oxides, sulfides, and carbides, as well as a small number of components of the "ice" group. Further uniting of the planetesimals resulted in the formation of planets of the Earth type and of asteroids.

The planets thus generated then had a long and rather complex thermic history, while the asteroids maintained their original composition and structure more or less unchanged. However, in the center of some of them there was considerable heating, apparently because of the decay energy of "short-lived" radioactive isotopes. In this process an iron-nickel core developed, which — when the asteroids broke up due to their collisions — led to the formation of iron meteorites, while stony meteorites were fragments of the peripheral part, or they were formed in the dissolution of asteroids which had retained their original composition and structure.

And so, according to the ideas which predominate most extensively, our planet was formed by the accumulation of cold solid bodies of inhomogeneous composition with differing contents of iron and silicates, but basically devoid of such free gases and volatile compounds as molecular hydrogen, light inert elements, and methane (Ref. 32). Because of the closeness of the region where the Earth was formed to the Sun, these gases had already left this region during

the formation of our planet and had accumulated in the colder regions of the protoplanetary cloud (e.g., in the region where Jupiter or Saturn formed). Only a certain quantity of these gases adsorbed by solid rocks were retained in the Earth which had been formed by now and entered its primordial atmosphere. atmosphere, however, could not be permanent, since the gases composing it were not retained by terrestrial attraction and dispersed into interplanetary space. Therefore, the Earth, having lost its primordial atmosphere, including a number of noble gases which were widespread in the universe, had on the whole acquired its present mass and the composition which is characteristic of it today, which /58 is very close to the composition of modern meteorites (Ref. 33). The age of the Earth matter which came into being in this way may be set at approximately 4.5 billion years.

The remaining compact mass of the Earth continued to evolve because of internal energy. In this process, this mass divided into core, mantle, and crust.

This event can date from a time more than four billion years ago. The mechanism for this type of differentiation of the initially uniform terrestrial substance still remains unclear. Most frequently, it is explained by advancing the hypothesis that there was a secondary melting of our planet because of initial gravitational heat and radiogenic heating. However, complete fusion of the Earth by this means would have required a period on the order of several billion years, while in fact the differentiation was able to run its course in an incomparably shorter period. An important role in complete or partial melting of the Earth was perhaps played by "short-lived" and now "extinct" isotopes like Be $^{10}$ , Al $^{26}$ , J $^{129}$ , Pu $^{244}$  and others.

In any case, the whole subsequent evolutionary course of our planet has been determined by its thermal history (Ref. 34). Climatic conditions on the Earth's surface now depend chiefly on the intensity of solar radiation and on the heat transfer of the irradiated surface. During formation of our planet, the principal sources of its internal heat were the gravitational energy evolved in agglomeration and contraction of the terrestrial matter and the energy formed in the decay of radioactive elements, whose change in time may be easily computed from the law of radioelement decay.

For our following discussion, the most important stage in the Earth's development was the formation on its surface of the crust, atmosphere, and hydrosphere.

The present terrestrial crust consists of granite and basalt mantles covered on the top with a casing of sedimentary rocks. The so-called mantle is located under the crust. It is characterized by ultra-basic rocks (dunites) poor in silicon.

On the basis of his experiments on zone melting of stony meteorites (chondrite), A. Vinogradov arrived at the conviction (Ref. 35) that the mantle dunites are remains which are left from the melting of the primordial substance of the Earth, which in its composition resembles that of chondrites. The melting of light basaltic rocks from the mantle under the effect of radiogenic heat had to be accompanied by the liberation of different vapors and gases due to their

vaporization as temperature rose or due to their formation in the solid terrestrial mantle as radioactive, radiochemical, and chemical processes occurred there.

<u>/59</u>

Therefore, formation of the aqueous and gaseous mantles of the Earth (its hydrosphere and atmosphere) was from the very beginning intimately associated with processes going on in the lithosphere.

The quantity of water on the Earth's surface in the first periods of our planet's existence must have been considerably less than at present. It is H. Urey's opinion that the primordial earth had only approximately 10% of the water in modern seas and oceans. The remaining water appeared later, gradually forming as the lithosphere developed from silica hydrates or in general from the water of constitution of the Earth's crust.

The age of the Earth's oceans may be approximately estimated from the content and rates of appearance of the separate chemical components, e.g., sodium or phosphorus. These estimates show the ocean's age to be about three billion years or more.

The age of the secondary atmosphere, produced from the gases liberated from the lithosphere, may be determined by its content of argon-40, which was formed during radioactive decay of the isotope potassium-40. A figure of from 4 to 3.5 billion years is derived (Ref. 36). Although during its formation the Earth was deprived of the greatest part of protoplanetary hydrogen which fell upon it, the abundance of hydrogen in the initial material nevertheless exerted a substantial effect on the subsequent composition of our planet and, in particular, its secondary atmosphere. Even after the loss of hydrogen as a free gas, the Earth was to retain a very large quantity of this element in the form of its compounds, many of which were liberated during formation of the Earth's crust into the atmosphere being created, and gave it a sharply-expressed reducing nature. Besides water vapor, we must mention ammonia, hydrogen sulfide, and gaseous hydrocarbons among these gases.

The molecular oxygen characteristic of the modern atmosphere was practically absent here. To be sure, under the influence of short-wave ultraviolat rays a certain decomposition of water vapor could proceed in association with volatilization of hydrogen and abiogenic formation of free  $0_2$  (Ref. 37). However, even in this case the oxygen could not accumulate in the atmosphere in any significant amounts, since it was very quickly and thoroughly absorbed by rocks which were unsaturated with it (Ref. 38).

We can even today observe this sort of  $0_2$  absorption process. Thus, for example, the masses of lava ejected onto the Earth's surface during present— /60 day volcano eruptions are usually very rich in metallic oxides. Coming into contact with the oxygen of the air, they begin intensive oxidation and seemingly burst into flame (acquiring a higher temperature than they had in the Earth's crust, emitting light, becoming more fluid, etc.).

The commonly known fact that ejected intrusive rocks (lavas, basalts) are black, grey, and green, while the sedimentary structures resulting from them (sands, clays) are yellow and red, is caused by the transformation of the iron

contained in the rocks from protoxides into oxides. Therefore, even now with the abundance of free oxygen in the atmosphere there is only enough to oxidize merely the most superficial layer of the Earth's crust. If all the green vegetation which continually replenishes the content of atmospheric oxygen should now disappear, then this atmospheric oxygen would also disappear in the course of some three or four millenia, being absorbed by the rocks which are unsaturated with it (Ref. 39).

Before the rise of green vegetation, so little free oxygen was formed abiogenically that rocks (including sedimentary rocks) could not be saturated by it to any degree, and the atmosphere must have been practically devoid of this gas. This secondary reducing atmosphere of the earth free of molecular oxygen lasted a rather long time. It may be confirmed even from direct geological data obtained from studying old Pre-Cambrian deposits.

Taking advantage of these data, M. Rutten (Ref. 40) divides the entire time which our planet has existed into two basic periods — the actualistic (similar to the present) and the preactualistic which preceded it. During these periods, the geological processes occurring on the Earth's surface differed profoundly from each other. As an illustration, we may cite the processes of rock weathering, at the basis of which lies the following pattern: (1) erosion of the original rock, (2) transportation of the resultant products, and (3) deposit of these products with the formation of sedimentary rock. In the present actualistic period, the chief role in the weathering of basic rocks is played by chemical processes in the presence of an atmosphere which is rich in free oxygen. The minerals which have already undergone oxidation are transported and deposited. The atmosphere of the preactualistic epoch, on the other hand, was reductive in nature, and therefore such minerals as feldspar, sulfites, etc. proved to be chemically resistant.

When transported, they were merely physically changed, but were deposited in chemically unchanged form. The fundamental works of K. Rankama (Ref. 41) investigating the old deposits of detrital rocks around the granite cliffs of Finland, the findings made by P. Ramdohr (Ref. 42) in studying the auriferous layers of the ancient mantles of South Africa, Brazil, and Canada, the data of H. Lepp and S. Goldich (Ref. 43) on the ancient deposits of iron ores in North America, Lorraine, and Luxemburg, and many others corroborate these statements.

From a study of these findings, M. Rutten arrives at the conclusion that all these structures may be formed only in a reducing atmosphere devoid of free oxygen and that therefore such an atmosphere must have been maintained on the Earth's surface until at least two billion years ago.

C. Sagan hypothesizes (Ref. 44) that signs of an oxidizing atmosphere appeared appreciably earlier, but on the basis of objective geological data Rutten demonstrates that an atmosphere rich in oxygen, like the present one, was formed only within a mere billion years. Between the dates which Rutten gives (two and one billion years), he thinks that there was a transitional era during which the Earth's atmosphere gradually became rich in free oxygen. This was associated with the development of life which had risen as early as the preactualistic epoch, as indicated by comparative biochemical and palaeontological data.

<u>/61</u>

To sum up all the above statements, the following chronological table of atronomical events leading to the formation of our planet may be given (Table 3).

TABLE 3. CHRONOLOGY OF ASTRONOMICAL AND GEOLOGICAL EVOLUTION

Event	Time Ago in Billions of Years
Formation of oldest stars in our galaxy	12–20
Formation of Heavy Elements	5.3
Formation of Sun and Planets of our System	5
Formation of the Earth in its Present Mass and Composition	>4.5
Differentiation of Earth matter, formation of Earth's Crust	>4
Formation of Oldest Known Minerals	3.6
Formation of the World's Oceans	>3
Formation of Secondary Reducing Atmosphere	>3.5
Geologically Determined Limit of Existence of Reducing Atmosphere	2
Formation of Oxygen Atmosphere of Modern Composition	1

How did the development of the carbon compounds — the narrower specific branch of the development of matter which is of special interest to us since it was the path by which life developed among us on Earth and on other similar celestial bodies — proceed against the background of these events?

As we saw above, carbon came into being even before the formation of the heavy elements, independently of the flares of supernovae in the stable process of stellar radiation. Therefore, it is an extremely widely disseminated element in space (Ref. 45). It is discovered by studying the spectra of all star classes, in particular those of the oldest generations. In stellar atmospheres of the highest temperature, carbon is present in the ionized or neutral atomic state (Ref. 46).

Here the conditions for formation of chemical compounds are still absent, but as soon as these conditions are created carbon immediately combines, chiefly with hydrogen, which could even be assumed a priori because of the exceptional quantitative predominance of hydrogen in space. In actual fact, compounds of carbon and hydrogen may be found in the most varied celestial objects under very diverse temperature and gravitational conditions.

Indications of these compounds may even be detected in the spectra of type A stars (Ref. 47). In the spectra of stars of the succeeding types, carbon bands appear with greater and greater clarity as the temperature of the stellar surface

<u>/62</u>

drops, and reach maximum distinctness in M and R spectra. Our Sun is, of course, a type G star (yellow star). Its atmospheric temperature is about  $6000^{\circ}$ C. Spectroscopic investigations demonstrate that carbon-hydrogen compounds in the form of methine (CH) are present on the Sun, and perhaps more complex compounds including several atoms of carbon and hydrogen (Ref. 48). In addition to this, a compound of carbon and nitrogen, cyanogen (CN), has also been detected on the Sun.

We therefore see that carbon-hydrogen compounds are widely distributed on the surface of stars having a temperature of several thousand degrees centigrade and of very high gravitation. On the other hand, however, we also find hydrocarbons at the opposite pole of thermal and gravitational conditions in interstellar gas-dust matter under extremely low gravitation and at temperatures close to absolute zero.

The studies of H. Kramers and D. ter Haar (Ref. 49) revealed the formation here of the simplest hydrocarbon radicals CH and CH $^{\dagger}$ . H. Urey states that, because of the catalytic action of dust and the abundance of hydrogen, in gas- /63 dust agglomerations free radicals must be converted into stable hydrocarbons. In fact, at the present time there has been direct proof of the presence of methane (CH $_4$ ) in cosmic gas-dust agglomerations, the prototypes of the material from which our solar system was created. (Ref. 50).

Occurrence of the simplest carbon compounds at a substantial distance from the stars under low-temperature conditions is also confirmed by findings on the chemical composition of comets (Ref. 51). These cosmic bodies are formed under the conditions of an almost interstellar medium (Ref. 52) somewhere near the orbit of Pluto, and from time to time penetrate the internal regions of our planetary system where their composition may easily be subjected to spectroscopic investigation. These investigations have shown that comets are teeming with light hydrocarbons, cyanogen, and carbon monoxide.

Within the limits of the solar system itself, we can discover huge quantities of methane in the atmosphere of the large planets — Jupiter, Saturn, Uranus, and Neptune (Ref. 53). The presence of methane in the atmosphere of Titan (a satellite of Saturn) arouses great interest (Ref. 54). Titan is forty times smaller than Earth in mass, but it can keep its methane atmosphere because of the very low temperature  $(-180^{\circ}\text{C})$  prevailing in its region.

Of particularly great significance for the question we are analyzing is the study of carbon compounds in meteorites -- first, because meteorites are still the sole non-terrestrial objects which we can examine directly not only chemically, but also mineralogically, and, second, because of the similarity of meteoritic matter with the material from which the Earth was formed (Ref. 55).

The problem of the origin of meteorites is under lively discussion in modern scientific literature. It is assumed that meteorites were formed in our solar system, principally between the orbits of Mars and Jupiter, in the zone of so-called small planets — the asteroids, which were apparently the "maternal bodies" for them.

A study of the various radioactive isotopes present in the meteorites enables us to date individual events in their history. The age of the heavy elements comprising them is the same as in other bodies of the solar system (about five billion years). From studying the isotopes of lead, rubidium and strontium, rhenium and osmium we can calculate the time which has elapsed since solidification of meteoritic matter as 4.5 billion years. The loss of certain volatile radiogenic isotopes (of helium and argon) indicates that the substance of some /64 meteorites could have been at a comparatively high temperature for a certain period. The time required for the formation of small fragments of major bodies (the so-called cosmic age of meteorites) has been established as merely tens or hundreds of millions of years by determining the isotopes which originated under the action of cosmic rays. The patterns followed by the composition and internal structure of the meteorites indicate the different conditions under which individual groups of meteorites differing in their chemical composition originated (Ref. 56).

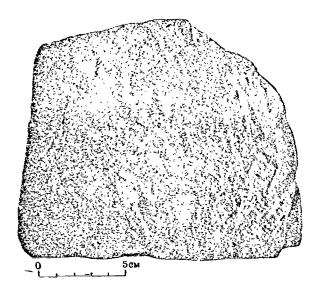


Figure 7. Carbonaceous Chondrite Mighei. Weight about 1600 Grams. (Collection of Commission on Meteorites of the Academy of Sciences USSR).

All meteorites are usually divided into two basic classes -- stony and iron. Iron meteorites consist principally of ferronickel (90% Fe, 8% Ni, 0.5% Co) and contain small quantities of phosphorus, sulfur, copper, and chromium. Carbon is represented in them chiefly in its native state or in combination with metals [cohenite --(FeNiCo)<sub>2</sub>C]. The structural features of these meteorites indicate that the ferronickel was previously in the melted state at a temperature above 1500°C, then in the process of very slow cooling over tens of millions of years crystallization and recrystallation of this alloy occurred. These meteorites are apparently fragments of the central part of the "parental bodies." The stony meteorites which fall more often on Earth were formed from the peripheral parts of these They contain significantly bodies. less iron, while silicates and oxides of such metals as magnesium, aluminum calcium, sodium, etc. predominate. Most stony meteorites contain no more 0.1-0.2% of carbon. But two types of

<u>/65</u>

meteorites are known whose carbon content is very high, fluctuating from 0.45 to 4.8%. These are carbonaceous diamantiferous achondrites (ureilites) and carbonaceous chondrites (Figure 7). The number of the latter in world meteorite collections is under ten, but they are of particular interest to us since the presence of certain minerals in them indicates that they were never heated higher than  $300^{\circ}$ C (Ref. 57).

Carbonaceous chondrites are rather brittle structures consisting of an opaque black mass in which tiny chondrules of a porphyrin nature and grains of olivine or of pyroxenes are disseminated.

Carbonaceous chondrites are characterized not only by a high carbon content, but also by water bound in the minerals (aqueous silicates and alumosilicates). The carbon in carbonaceous chondrites is represented by an amorophous carbon material and graphite. It also enters into the composition of organic materials and carbonates. The adsorbed gases contain  ${\rm CO_2}$ ,  ${\rm CH_4}$ ,  ${\rm CO}$ , and  ${\rm H_2}$ , as well as Ar, The organic substances are chiefly represented by hydrocarbons, partially oxidized and containing sulfur. Along with low-molecular hydrocarbons, carbonaceous chondrites also contain polymerized compounds, principally of the aliphatic series (Ref. 58). In the scientific literature reports have appeared on the discovery in meteorites even of such complex compounds as pyrimidine bases or amino acids (Ref. 59), but these reports still need further experimental verification (Ref. 60). G. Mueller, after analyzing in detail all presently known facts from the field of chemistry and petrography of both the inorganic and organic phases of carbonaceous meteorites and after weighing all data on their origin, concludes that the carbon compounds in these meteorites undoubtedly arose during chemical development in a manner quite unrelated to life. The abiogenic origin of the meteoritic organics is likewise corroborated by the recent work of M. Briggs studying the organic polymer substances in carbonaceous chondrites (Ref. 62). Research of this sort is of great interest, since it spreads out before us the ways of studying the abiogenic formation of organic substances under natural conditions which, to be sure, are somewhat different from those which prevailed on Earth before the development of life upon it.

Below we will return to the investigations, extensively developed at present, on these substances in meteoritic material when we discuss the question of ways <u>/66</u> that organic polymers arose during the evolution of cosmic bodies (see Chapter III). Here, however, we would only like to stress the thesis that we are able to confirm the formation of carbon compounds -- principally in the reduced form of carbon -- as hydrocarbons, in the most diverse objects of our stellar universe (in the stars, in clusters of gas-dust matter, planets and their satellites, in comets and meteorites).

Most of the celestial objects listed have developed, and are developing, along different paths from our own planet, but, as we have seen, the occurrence of the most primitive carbon compounds and their initial evolutionary stage are extraordinarily universal in the world which surrounds us. We may assure ourselves that in this respect the Earth is no basic exception by acquainting ourselves with the development of carbon compounds during the formation of our planet.

As we indicated above, still long before the formation of the Earth as a planet, from that part of the protoplanetary discoidal cloud where it was formed the gaseous component of this cloud (hydrogen and the noble gases) had to be volatilized, and the substances comprising the "ice" group also must have partially disappeared. This applies particularly to methane, which still stays in the gaseous state at very low temperatures.

F. Aston forty years ago first drew attention (Ref. 63) to the low content of noble gases in the Earth's composition, and explained this by their chemical inertness, their incapability of binding themselves to other elements into heavier molecules. H. Suess (Ref. 64) and H. Brown (Ref. 65) later pointed out that the concentration of noble gases in the composition of the Earth is very greatly reduced as compared with their concentration in the cosmos. The abundance of noble gases was greatly "depleted" by their volatilization out of that part of the protoplanetary cloud in which the Earth formed. H. Urey gives a table (Ref. 66) which gives data on the relative content in the cosmos and on Earth of certain elements and their compounds. This particular table indicates the degree of the "depletion factor" in comparison to xenon and the fraction of gas or element which was preserved in the Earth from their total concentration in the gas-dust cloud (Table 4).

TABLE IV. "DEPLETION FACTOR" FOR VOLATILE ELEMENTS AND COMPOUNDS ON EARTH

Elements and Compounds	Relative Content in Space (Si = 10,000)	Moles/cm <sup>2</sup> on Earth	"Depletion" in Comparison to Xenon	Fraction Remaining on Earth
Ne 	166,000	6.5 • 10 - 4	0.9.10-4	0.9.10-11
Ar <sup>36+38</sup>	1,120	1.2.10-3	2.6.10-2	2.6.10-9
Kr	0.718	3.5.10-5	1	1.0.10-7
Xe	0.0665	2.8.10-6	1	1.0.10-4
H <sub>2</sub> 0	111,000	15,000	3,200	3.0.10-4
C	40,000	350	210	2.0.10-5
N	80,000	54	16	1.6.10-6

Table 4 makes clear that the content of volatile elements and compounds is substantially "depleted," as compared to the non-volatile ones. Since this division was accomplished even before the Earth condensed into a solid body, it proceeded under the conditions of a very low gravitational field. It is therefore understandable that the neon content was "depleted" to a significantly greater degree than that of xenon, but the amount of water and of carbon and nitrogen compounds is abnormally high in terms of these conditions. If "depletion" had taken its entire course by mass fractionation — i.e., if

<u>/67</u>

volatilization from the gravitational field had taken place by molecular weight — then CH<sub>4</sub> would have had to become "depleted" to the same degree as neon. If, however, "depletion" had moreover depended on vapor pressure, solubility, adsorption, or formation of hydrates, then the "depletion factor" for CH<sub>4</sub> should have been between the values for argon and krypton, but the fact is that a far greater portion of carbon has been preserved on Earth.

The sole acceptable explanation for such a great carbon concentration on Earth is the hypothesis that the carbon was retained in the form of certain chemical compounds heavier than methane during the formation of our planet. Such compounds were indisputably the metal carbides, graphite, or amorphous carbon which we may detect in meteorites, but organic compounds to a certain degree also may have played the role of the form in which an appreciable portion of the initial carbon was maintained in the Earth's composition. This is indicated by the discovery of organic compounds of that type in carbonaceous chondrites.

<u>/68</u>

On this subject many authors are at present expressing the opinion that a substantial quantity of organic substances must have been synthesized even before the formation of the Earth as a planet. Thus, for example, L. Lederberg and D. Dowier (Ref. 67) believe that organic compounds were formed under the effect of corpuscular radiation ever in particles of the parent cosmic dust. Fowler, Greenstein, and Howle (Ref. 68) also underscore the great significance of the formation of organic compounds in the dust cloud from which the Earth was formed. J. Glasel in experiments on models (Ref. 69) synthesized acetylene, ethane, propane, and several other hydrocarbons by bombarding CH<sub>4</sub> at a low temperature with electrons. R. Berger demonstrated that urea, acetamide, and acetone are synthesized from CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O at 77 K (-196 C) as the result of high-energy proton action. Many other such examples may also be presented.

The present extensive research on organic substances in carbonaceous chondrites, as well as certain data on the nature of "noctilucent clouds" and meteoritic dust in red oceanic clays impelled J. Bernal (Ref. 70) to formulate his new hypothesis of the cosmic origin of the organic substances which served as the material for formation of living beings on Earth. This hypothesis states that the synthesis of more and more complicated organic molecules and their polymers was already going on in particles of cosmic dust covered with ice and condensed gases under the influence of solar radiation and the action of cosmic rays. With an increase in temperature, in the zone where planets of the terrestrial type were formed, the surface ice and condensation layers vaporized and volatilized, but the more or less high-molecular organic substances were kept to provide thereafter the beginning for the formation of the carbon complexes which may now be detected in carbon meteorites. The Earth, formed by the agglomeration of chondritic bodies at a relatively low temperature, received from them the already finished complex of organic substances, a portion of which could have appeared on the planet's surface in comparatively unchanged form and would have served as the basis for the subsequent development of life. The feasibility of this sort of synthesis of organic substances in cosmic dust particles is corroborated in a number of the above-mentioned facts.

S. Miller and H. Urey, however, believe (Ref. 71) that if organic substan- /69 ces of more or less complex composition were synthesized in particles of the parent substance even before the Earth had condensed into a solid body, they would automatically have been able to play a decisive role during the development of life on the surface of our planet.

When the Earth was formed from the planetisimals, the organic substances must have been more or less uniformly distributed throughout its whole mass, and it is very doubtful that they left through the surface in unchanged form. Even if our planet did not completely melt, its internal temperature — owing to gravitational energy and radioactive heating — was quite sufficient to pyrolyze the organic compounds in its interior. Only products of this pyrolysis (like  $\mathrm{CH_4}$ ,  $\mathrm{CO_2}$ ,  $\mathrm{CO}$ ,  $\mathrm{N_2}$ ,  $\mathrm{NH_3}$ ,  $\mathrm{H_2O}$ , and  $\mathrm{H_2}$ ) could be liberated on the surface of the Earth and enter into the composition of its secondary atmosphere since most of them (excepting  $\mathrm{H_2}$ ) were already retained by the terrestrial attraction of the compact planet which had been formed. A significant part of the carbon dioxide ( $\mathrm{CO_2}$ ) of the secondary atmosphere interacted with the silicates of the lithosphere and was deposited in the Earth's crust in the form of carbonates, deposits of which had already arisen long before the appearance of life. The reduced forms of carbon and nitrogen ( $\mathrm{CH_4}$  and  $\mathrm{NH_3}$ ) served as material for the secondary formation of organic substances which became ever more complex.

As we pointed out above, however, the carbon compounds retained during the Earth's formation could be not only organic compounds more complex than methane, but also amorphous carbon, graphite, and metal carbides. These latter, interacting with hydrated rocks, had to produce gaseous hydrocarbons on a large scale on the surface of the Earth. A source of hydrocarbons in the formation of the Earth's crust was also native carbon in its interaction with the hydrogen produced by radiochemical decay of water. Therefore, the liberation of hydrocarbons and their closest derivatives onto the Earth's surface during formation of the lithosphere not only could, but also had to, be effectuated in numerous ways: (1) by interaction of carbides with hydrated rocks; (2) by direct reduction of graphite and amorphous carbon by the free hydrogen produced in radiochemical decay of water; (3) in pyrolysis of the primary organic substances; (4) in the liberation of primordial methane adsorbed by rocks; and so on.

At present, we can only argue about which of the abiogenic formations of hydrocarbons was general at the time of the Earth's own formation, and in the sub- /70 sequent eras of its existence. But the necessity of this formation itself is not doubted at all in our time. It is also corroborated by several geological finds which have now been directly discovered.

The formation of our planet's crust, which began in the early periods of the Earth's existence, is not finished even in our day. The result of this is that abiogenic formation of hydrocarbons is proceeding at several spots on the globe even today (Ref. 72). This is indicated, in particular, by a number of gas deposits which have no direct connection with sedimentary rocks. Such, for example, are the hydrocarbon-type gases which form in the crystalline rocks around Lake Huron in Canada or in the Ukhta Field in our country, where

hydrocarbons may be discovered in very large quantity in the cracks in igneous rocks. A report by V. Sokolov (Ref. 73) states that he discovered methane, ethane, propane, and higher-molecular hydrocarbons in igneous rocks at a number of locations in the Soviet Union.

Of substantial interest in this respect are the gas deposits recently discovered in the Khibinskiy Massif of the Kola Peninsula. Analysis of them shows that they contain methane and heavier hydrocarbons. Very careful examination of the physicochemical and geological situation here, moreover, points to the magmatic origin of these gases (Ref. 74).

The number of discoveries of petroleum in igneous and metamorphic rocks continues to grow, although relatively little attention is yet paid to them because they rarely are of industrial significance. Nevertheless, they are now counted in the hundreds (Ref. 75). In particular, liquid and gaseous hydrocarbons in the form of smears and insignificant deposits were also discovered in deep boring along cracks in metamorphic and crystalline foundation rocks, to which they could scarcely have penetrated from sedimentary rocks.

Therefore, although the petroleum extracted from sedimentary deposits clearly bears traces of its biogenic origin, in the light of the facts presently known, we cannot deny the existence of abiogenic processes of hydrocarbon formation, even in the modern era of our planet's existence.

R. Robinson in a detailed study (Ref. 76) of different petroleum specimens obtained from numerous deposits directs attention to the content of substances /71 far removed from biochemical compounds in crude petroleum of more ancient origin. The formation of these substances from biological material has no rational explanation which is acceptable chemically or geologically. On the contrary, the fact that they were formed abiogenically seems easily understandable and experimentally reproducible under close to natural conditions. Therefore, Robinson comes to the conclusion that petroleum has a dual (abiogenic and biological) origin. Moreover, he convincingly demonstrates the fact that the more ancient the petroleum is, the more indications it displays of its abiogenic origin.

Therefore, we can now scarcely doubt but that in the initial periods of the Earth's existence, a substantial quantity of hydrocarbons, which also were initial materials for subsequent development of organic substances, were present on its surface (in its atmosphere and hydrosphere).

The bulk of these hydrocarbons originated during formation of the Earth's crust and, so to speak, were of endogenic origin. Recently, however, more and more papers have been appearing to point out that our planet throughout its whole existence has been "fed" with organic substances coming from outside exogenically. Of particularly great significance in this respect have been the meteorites falling on the Earth's surface, especially the carbonaceous chrondites (Ref. 77). The organic substances contained in them must not have been subjected to severe heating and pyrolysis. This means that these hydrocarbons could play a role in the subsequent syntheses of complex organics which were carried out on the surface of the Earth. Recently J. Oro advanced the hypothesis (Ref. 78) that, along with the organic substances of the Earth which were geochemically produced on it, a considerable portion of organic substances were

brought to our planet not only by meteorites, but also by comets.

According to H. Urey's calculations (Ref. 79), during the life of our planet, no less than 100 direct collisions must have occurred between the Earth and comets, whose matter remained in the Earth's atmosphere and increased its content of primary substances. Oro computed that, merely as a result of this, the Earth in the first two billion years of its existence must have received from  $2\cdot10^8$  to  $1\cdot10^{12}$  metric tons of comet material consisting chiefly of carbon compounds. As a matter of fact, however, in Oro's opinion the mass of comet material captured by the Earth must have been considerably greater still, since the material of comets which avoided a direct collision, but passed sufficiently close to the Earth, might be added to this (Ref. 80).

The fall of the so-called Tunguska meteorite in 1908 can serve as a graphic /72 illustration of a collision between a comet and the Earth. As V. Fesenkov has recently demonstrated (Ref. 81), the body which fell to Earth in the sight of many eye witnesses, felling enormous numbers of trees on the taiga and remaining a mystery for a long time was indeed not a meteorite, but the nucleus of a comet which was retarded in the Earth's atmosphere at a height of 6 to 7 kilometers and therefore created a powerful blast wave. A very essential fact is that comets abound not only with light hydrocarbons, but also with cyanogen (Ref. 82). Therefore, even this simplest carbon-nitrogen compound must have entered into the composition of th original carbon compounds, which greatly increased the possibilities of their further development.

S. Miller and H. Urey, according to computations which they conducted (Ref. 71), believe that the portion of organic substances brought with comet material is very small. It is their opinion that this portion amounts to approximately one ten-thousandth of the quantity of organics formed on the basis of the Earth's crust. Nor could meteorites provide an adequate amount of carbon compounds. Obviously, therefore, the bulk of the original hydrocarbons necessary for the genesis of life and their closest derivatives were after all formed endogenically on the surface of the Earth during the formation of the Earth's crust. We may form a concept of the subsequent evolutionary course of these substances by experimentally reproducing the conditions which existed at one time on the surface of the primordial Earth and by studying how transformation of the original hydrocarbon compounds proceeded under these conditions.

## REFERENCES

- 1. Russel, R., Farquhar, R. Lead Isotopes in Geology Interscience. N. Y.-London, 1960.
- 2. Vinogradova, A., Tugarinov, A. Geokhimiya, No. 9, p. 723, 1961.
- Kulp, Y. International Geological Congress, Report of 21st Session, Norden, 1960. Gen. Editor T. Sorgenfrei, Part 3. Edit. F. Wickman and E. Welin, p. 18. Copenhagen, 1960.
- 4. Anders, E., Goles, G. Journal Chemical Education, V. 38, 58, 1961.
- 5. Anders, E. In "The Moon, Meteorites and Comets", Ed. G. Kuiper and B. Mid-dlehurst, p. 402. Chicago, 1963.
- 6. Patterson, C. Nuclear Processes in Geological Settings II. Pennsylvania State University, NAS-NRS, Pub. No. 400, p. 157, 1955.

- 7. Whipple, F. Geochim. et Cosmochim Acta, 10, 230, 1956. Proceedin. Nation. Acad. Sci. USA, V. 52, p. 568, 1964.
- 8. Rutherford, E. Nature, 112, 305, 1923.
- 9. Fowler, W. Proceedin. Nation. Acad. Sci. USA, V. 52, 524, 1964.
- 10. Baranov, V., Knorre, K. Meteoritika, Issue 21, 1961.
- 11. Anders, E. Rev. Modern Physic., 1961.
- 12. Reynolds, I. Phys. Rev. Letters, 4, 8, 1960.
- 13. Greenstein, I. Proceedin. Nation. Acad. Sci. USA, V. 52, p. 549, 1964. /73
- 14. Fowler, W. Ann. Physics, V. 10, N. 2, 1960.
- 15. Hoyle, F. Observatory, Feb., 1962.
- 16. Brownlee, R., Cox, A. Sky and Telescope, 21, 251, 1961.
- 17. Hoyle, F., Fowler, W., Burbridge, G, Burbridge, E. Astrophys. J., 139, 909, 1964.
- 18. Struve, O. Communications presentées au neuvième Colloque International d'Astrophysique tenu à Liège les 6, 7 et 8 Juillet 1959 sous la Présidence du professeur S. Rosseland (Reports Presented to the Ninth International Astrophysics Colloquium Held at Liege on 6, 7, and 8 July,1959, Under the Chairmanship of Professor S. Rosseland). Memoires in 8 vo. de la Société Royale des Sciences à Liège 5th Series, V. 3, Joint Session Inst. d'Astrophysique, 1959.
- 19. Cameron, A. Ibid.
- Greenstein, J. Science in Progress. Ed. W. Brode, Yale Univer. Press, p. 173, 1963.
- 21. Fesenkov, V. Priroda, 10, p. 2, 1964.
- 22. Frank-Kamenetskiy, D. Priroda, 11, p. 17, 1963.
- 23. ter Haar, D., Cameron, A. Origin of the Solar System. Ed. R. Yastrow and A. Cameron. New York, p. 4, Acad. Press, 1963.
- 24. Shmidt, O. Chetyre lektsii o teorii proiskhozhdenii Zemli (Four Lectures on the Theory of the Origin of The Earth). 3rd ed. Izdatel'stvo Akademii Nauk SSSR, 1957.
- 25. Shauman, E. Voprosy kosmogonii (Problems in Cosmogony). Vol. 3, 227. Izdatel'stvo Akademii Nauk SSR, 1954.
- 26. Goldberg, L., Muller, E., Aller, L. Ap. J. Suppl., 5, No. 45, 1, 1960
- 27. Brown, H. Ap. J., 111, 641, 1950; Brown, H., Ingraham, M. Phys. Rev., 72, 347, 1947.
- 28. Goldberg, L., Muller, E., Aller, L. Ap. J. Suppl., 5, No. 45, 1, 1960.
- 29. Suess, H. In Summer Course on Nuclear Geology. Varenna, p. 28, 1960; Khil'mi, G. 200 let nuchnoy kosmogonii (Two Hundred Years of Scientific Cosmogony). Izdatel'stvo 'Znaniye," Moscow, 1955.
- 30. Hoyle, F. Quart. J. Roy. Astron. Soc., 1, 28, 1960.
- 31. Urey, H. In "Space Science". Ed. D. Le Galley, p. 4, N. Y., John Wiley and Sons, 1963.
- 32. Urey, H. The Planets, Their Origin and Development. Yale Univ. Press., New Haven, 1952.
- 33. Urey, H. Hugo Muller Lecture. Proc. Chem. Soc., March, 1958.
- 34. Baranov, V. Thermal History of the Earth, In Collection: Vozniknoveniye zhizni vo Vselennoy (Origin of Life in the Universe). Izdatel'stvo Akademii Nauk SSSR, p. 22, 1963.
- 35. Vinogradov, A. Geokhimiya, No. 1, p. 3, 1961; Ibid, 3, p. 269, 1962.
- 36. Kharley, P. Vozrast Zemli (The Age of the Earth). Fizmatizdat, 1962.
- 37. Harteck, P., Hensen, I. Z. Naturforsch, 3a, 591, 1948.
- 38. Latimer, W. Science, 112, 101, 1950; Moses, E., Ta-You-Wu. Phys. Rev.,

- 83, 109, 1951.
- 39. Goldschmidt, V. Skriften Norske Vidensk. Ac. Oslo, 1, Matnaturvid. kl, N. 4, 1937.
- 40. Rutten, M. The Geological Aspects of the Origin of Life on Earth. Elsevier. Amsterdam, 1962.
- 41. Rankama, K. Geolog. Soc. Am. Spec. Paper, 62, 651, 1955.
- 42. Ramdohr, P. Abhandl. Deut. Akad. Wiss. Berlin, Kl. Chem. Geol. und Biol., 3, 35, 1958.
- 43. Lepp, H., Goldich, S. Geol. Soc. Am. Bull., 70, 1637, 1959.
- 44. Sagan, C. Rad. Research, 15, 174, 1961.
- 45. Merrill, P. Linii khimicheskikh elementov v astronomicheskikh spektrakh (The Lines of Chemical Elements in Astronomical Spectra). Fizmatizdat, 1959.
- 46. Plaskett, I. Publ. Dom. Astrophys. Obs. Ottawa, 11, N. 16, 72, 1924.
- 47. Waterman, E. Lick Obs. Bull., 8, 1, 1913.
- 48. von Klüber, H. Das Vorkommen der chemischen Elemente im Kosmos (The Occurrence of Chemical Elements in the Cosmos). Borth. Leipzig, 1931.
- 49. Kramers, H., ter Haar, D. Bull. Ast. Inst. Netherlands, 10, 137, 1946. /74
- 50. Bates, D., Spitzer, L. Astrophys. J., 113, 441, 1951.
- 51. Whipple, F. Nature, 189, 127, 1961.
- 52. Donn, B., Urey, H. Astrophys. J., 123, 339, 1956.
- 53. Adel, A., Slipher. Physic. Rev., 46, 902, 1934.
- 54. Kuiper, G. Astrophys. J., 100, 378, 1944.
- 55. Krinov, E. Meteorites. London Pergamon Press, 1960. Principles of Meteorites. London Pergamon Press, 1960.
- 56. Urey, H. Nature, 192, 1119, 1962.
- 57. Kvasha, L. "Carbonaceous Chondrites," In the Collection: Vozniknoveniye zhizni vo Vselennoy (Origin of Life in the Universe). Izdatel'stvo Akademii Nauk SSSR, 1963; Masson, B. J. Geophys. Res., 65, 2969, 1960.
- 58. Vdovykin, G. Geokhimiya, p. 135, 1962; In the Collection: Vozniknoveniye zhizni vo Vselennoy (Origin of Life in the Universe). Izdatel'stvo Akademii Nauk SSSR, 1963.
- 59. Vanghn, S., Calvin, M. North-Holland Publishing Co., Amsterdam, 1960 Calvin, M. Chemical Evolution. Coudon Lectures, 1961.
- 60. Vallentyne, S. Quoted from S. Fox, "The Origin of Prebiological Systems". Acad. Press, 1965.
- 61. Mueller, G. Advances in Organic Geochemistry, p. 119. Monogr., N. 15. Earth Science Series, Ed. E. Ingerson, Pergamon Press, 1964.
- 62. Briggs, M. Life Sciences, N. 1, p. 63, 1963.
- 63. Aston, F. Nature, 114, 786, 1924.
- 64. Suess, H. J. Geology, 57, 600, 1949.
- 65. Brown, H. The Atmosphere of the Earth and Planets. Ed. G. Kuiper, Univ. Chicago Press, p. 258, 1949.
- 66. Urey, H. Astrophys. J., Suppl. 1, 147, 1954.
- 67. Lederberg, L., Dowier, D. Science, 127, 1473, 1958.
- 68. Fowler, W., Greenstein, J., Hoyle, F. Amer. J. Physics, 29, 393, 1961. Geophys. J. Roy. Astron. Soc., 6, 148, 1962.
- 69. Glasel, I. Proc. Nat. Acad. Sci. USA, 47, 174, 1961.
- 70. Bernal, J. Biochemical Horizons. Izdatel'stvo "Mir," 1964. In the Book: The Origin of Prebiological Systems, Ed. S. Fox. Academ. Press., N. Y., 1965.
- 71. Miller, S., Urey, H. In the Collection: Problems in Evolutionary and Technical Biochemistry. Ed. V. Kretovich. p. 357, 1964.

- 72. Kropotkin, P. In the Collection: Vozniknoveniye zhizni na Zemle (Origin of Life on Earth). A. I. Oparin, Ed. Izdatel'stvo Akademii Nauk SSSR, p. 88, 1959.
- 73. Sokolov, V. Ibid., p. 59, 1959.
- 74. Petersil'ye, I. Geokhimiya, 1, p. 15, 1962.
- 75. Kropotkin, P. See Sovetskaya Geologiya, Collection 47. Gosudarstvennoye Nauchno-Technicheskoye Izdatel'stvo, p. 104, 1955.
- 76. Robinson, R. Advances in Organic Geochemistry Mon., N. 15. Earth Science Series, p. 7, 1964.
- 77. Bernal, J. Transactions of the Fifth International Biochemical Congress. Symposium III. A. I. Oparin, Ed., p. 9, 1962.
- 78. Oro, J. Nature, 190, 389, 1961.
- 79. Urey, H. Nature, 173, 556, 1957; Fesenkov, V. Sci. Amer., 204, 180, 1961.
- 80. Opik, E. Irisch. Astron. J., 4, 84, 1956; O'Keefe, J. J. A. Science, 133, 562, 1961.
- 81. Fesenkov, V. Astronomicheskiy Zhurnal, No. 5, 1961.
- 82. Swings, P., Haser, L. Atlas of Representative Cometary Spectra Universit. of Liège Astrophys. Institute, Louvain.

## III. FORMATION OF THE "PRIMARY BROTH"

/75

How can we discover the paths of chemical evolution taken by the carbon compounds which formed endogenically on the Earth's surface or were brought to our planet by meteorites and comets even long before the development of life on Earth?

At first glance it may seem that the most direct and reliable answer to this question should be given by geological and geochemical research — direct discovery and study under natural conditions of the transformations of carbon compounds which, perhaps, may even now be in the process of abiogenic formation somewhere with no immediate connection with the vital activity of organisms. Right at this very moment, carbonic gases produced inorganically in the formation of the Earth's crust are continually being introduced into our atmosphere. Meteorites and comets continue to "feed" the Earth with carbon substances just as in the remote past, and the waters of the modern ocean also contain a small quantity of diverse organic substances. True, these substances were biogenically produced here by the decay of marine organisms, but, perhaps, somewhere in the ocean's depths in the absence of living creatures they are again undergoing an evolution similar to that which went on at some time on the primordial lifeless Earth. We can become acquainted with this evolution by studying it now directly <a href="#">/76</a> under natural conditions.\*

Everything that we know on this subject, however, causes us to be grievously disappointed in the possibility that such a direct frontal attack can be mounted against the problem which we are investigating. Although geochemical investigations are of a certain interest in solving it, the results of these investigations

<sup>\*</sup>J. Keosian has recently given expression to the idea that the formation of life often repeats itself and is going on even now (see his book, <u>The Origin of Life</u> [Ref. 1]).

must not be mechanically transferred to phenomena which went on in the preactualistic era and must not be directly utilized to judge the processes taking place on the surface of the Earth during the initial periods of its existence.

There is no doubt but that the abiogenic transformations of carbon compounds which preceded the appearance of life were effectuated on the surface of the Earth (in its atmosphere and hydrosphere) under conditions which were still profoundly different from modern ones. These differences reduced basically to the following intimately-interconnected circumstances:

- 1. The absence around the primordial Earth of the radiation belt which, according to R. Uffen's findings (Ref. 2), resulted from movements in the terrestrial crust approximately 2.5 billion years ago. Before that, the corpuscular solar radiation could freely reach the Earth's surface.
- 2. The lack of free oxygen in the preactualistic atmosphere. This excluded the possibility of direct and deep oxidation of reduced carbon compounds.
- 3. Abundance of shortwave ultraviolet radiation penetrating the whole atmosphere and reaching the Earth's surface. This created far greater possibilities for abiogenic photochemical processes than for those which take place solely with the longer-wave radiation which is accessible to the Earth's surface in the modern era.
- 4. The absence of living organisms with their perfected metabolism which rapidly draws varied organic compounds into its sphere of influence.

We do not at the present time have such conditions on the Earth's surface in the natural environment. The ionizing particles ejected by the Sun are for the most part detained at present by the magnetic field of the Earth and are deflected to form the radiation belt. The whole terrestrial globe is surrounded at an altitude of 30 km above its surface by an ozone screen which bars the access of shortwave ultraviolet radiation to us. The atmosphere, the top layer of the ground, and the entire hydrosphere are very rich in free oxygen. As recent investigations aboard the Soviet expeditionary vessel Vityaz' have demonstrated (Ref. 3), even the waters of the deepest depressions in the Pacific Ocean are to a great degree saturated with  $0_2$ . We are able to discover reducing conditions only in very rare and exceptional cases, e.g., in the fjords of Norway.

But here, too, as everywhere, these waters are rich in organisms, anaerobic microbes in particular, and we are unable to study abiogenic processes when organisms are present. In this respect the organisms "confuse all our charts." They excrete into the external inorganic medium specific inorganic substances which can be formed only in highly organized metabolism and, on the other hand, the organisms absorb and consume other substances, drawing them into their metabolism which, of course, did not exist in the primordial abiogenic medium.

As we now know, Charles Darwin was writing about this in one of his letters (Ref. 4): "It is often said that at present all conditions exist for the primordial formation of living organisms. But if (and, ah! what a big "if"), we

<u>/7</u>7

could imagine that in some small, warm body of water containing all sorts of ammonia and phosphorous salts, light, heat, electricity, etc., a protein substance was created capable of experiencing further, more complex transformations, then at the present time such a substance would have to be consumed or absorbed, which could not happen in the period preceding the formation of living creatures."

Therefore, although at first glance it may appear paradoxical, we must acknowledge that the basic reason that the primordial formation of life is at present impossible under natural conditions is that it has already come into being. Therefore, due to this fact a drastic change in conditions has occurred on the Earth's surface, and this change excludes the possibility of any prolonged evolution of organic substances along the same paths traversed by this evolution in the preactualistic era of the Earth's existence.

We are thus forced to construct our ideas of this primordial evolution chiefly on the basis of laboratory experiments in which we attempt artificially to recreate the physical and chemical conditions which at one time prevailed on the Earth's surface.

In so doing, we take our start from the common conviction that the chemical potentialities of methane or another organic substance are unchanged now as in the past, both in the primary or secondary terrestrial atmosphere and in the modern chemist's flask, although these potentialities will be realized differently, depending on the particular conditions of the surrounding medium. Therefore, by consciously reproducing experimentally the conditions of the preactualistic era we are justified in expecting results upon the basis of which we will be able to form an idea of events in the remote past. It is of course necessary at the same time also to take advantage of any opportunities to compare our conclusions with the facts which may be derived from studying natural substances and phenomena, not only on the surface of the Earth, but also on meteorites and other celestial bodies.

The extensive data accumulated at present by organic chemistry indicate the exceptionally high reactive capacity of hydrocarbons and their closest derivatives (Ref. 5).

From as early a time as that of Carl Schorlemmer (Ref. 6) all modern organic chemistry has been regarded as the chemistry of hydrocarbons and their derivatives, because latent in these compounds are chemical potentialities which are striking and unique. There is no doubt whatever but that the hydrocarbons present on the surface of our planet must have extensively exploited these potentialities during those many hundreds of millions of years which separated the period of the Earth's formation from the moment that life appeared thereon.

Under the conditions of the preactualistic period, they were able to interact with each other and with the water vapor, ammonia, hydrogen sulfide, and other gases of the secondary reducing atmosphere of the Earth, and to form a variety of complex compounds which is entirely foreign to inorganic nature. These interactions of hydrocarbons and their derivatives could come about spontaneously in the preactualistic atmosphere and hydrosphere because of the intrinsic potential energy of the reduced carbon compounds, while the rate of reactions of this type depended greatly on the presence of particular inorganic

catalysts.

A good illustration of this statement may be considered the recently published and very thorough article by C. Bird (Ref. 7) which lists numerous organic syntheses catalyzed by metals that Bird believes could also have taken place on the primordial Earth.

An important role in the organochemical reactions of that time, however, must also have been played by external energy sources -- primarily shortwave ultraviolet light, then radioactive radiation from the Sun and the Earth's interior, spark and silent discharges in the atmosphere, and, finally, the high temperature of volcanic eruptions.

S. Miller and H. Urey (Ref. 8) give the following data (Table 5) on the energy sources accessible to the primitive terrestrial surface which could be utilized for primordial abiogenic syntheses.

TABLE 5. ENERGY SOURCES FOR CASES OF PRIMORDIAL ABTOGENIC SYNTHESIS

OF PRIMORDIAL ABIOGENIC SYNTHESIS				
(kal/cm <sup>2</sup> year)				
1.	. Solar ultraviolet light:			
	2500 Å	570		
	2000 Å	85		
	1500 Å	3.5		
2.	Electrical Discharges	4.0		
3.	Ionizing radiation	0.8		
4.	Heat of Volcanic Eruptions	0.13		

This table very roundly presents the numerical relationship of the different energy sources, but takes inadequate account of cosmic ray energy and - energy of chargedparticles emitted by the Sun. At the present, the greater part of ionizing particles of this sort are held back by the Earth's magnetic field. However, before formation of the radiation belt in the preactualistic era the magnitude of this energy source was far greater than it is now. Therefore, a very significant role in cases of prebiological syntheses of organic substances on Earth must also be attributed to ionizing radiation.

The utilization of these sources of energy under the artificial conditions of the laboratory, which imitate the conditions of the primitive surface of the Earth, has made it possible in many experiments to synthesize various, some-

times very complex, biologically important substances. The initial materials for these syntheses were such primitive compounds as methane, ammonia, and water vapor, as well as certain very close derivatives easily occurring in them, as, for example, CO, HCN, formaldehyde, acetaldehyde, thiourea, ammonium thiocyanate, etc. The total number of papers published in this area is now very large. The result of this work was to derive organic acids and aldehydes, amino acids and polypeptides, amines and amides, sugars (in particular ribose and deoxyribose), purine and pyramidine bases, nucleosides and nucleophosphates, polynucleotides, porphin-like substances, and other biologically important compounds. Many of these papers were reported at the Moscow Symposium on the Formation of Life on Earth in 1957 (Ref. 9) and at the Florida Conference on the Rise of Prebiological Systems in 1963 (Ref. 10).

<u>/79</u>

They are summarized in a detailed article by T. Pavlovskaya and A. Pasynskiy (Ref. 11), as well as in the recently published survey by the same authors (Ref. 12). Therefore, we may restrict ourselves here to pointing out merely the most /80 important research, chiefly that on protein and nucleinic components.

The basic data on amino-acid formation under the effect of electric discharges in a gaseous mixture similar to the possible composition of the primary atmosphere of the Earth were derived as far back as 1953 in S. Miller's famous paper (Ref. 13). Under the action of spark and silent discharge on a mixture of  $CH_4$ ,  $NH_3$ ,  $H_2$ , and water vapors for a week with the mixture constantly circulating (Figure 8), it was discovered by Miller that glycine, alanine,  $\alpha$ -aminobutyric and  $\alpha$ -aminoisobutyric acids,  $\beta$ -alanine, aspartic and glutamic acids, sarcosine, and  $N-CH_3$ -alanine formed in it. The intermediate reaction products were aldehydes and HCN.

Miller's findings were corroborated in the work by T. Pavlovskaya and A. Pasynskiy (Ref. 14) which employed a somewhat different apparatus, while the excess amount of hydrogen was exchanged for CO. The appropriateness of this substitution was based on thermodynamic calculations. Subsequent papers by these authors experimentally demonstrated the sterility of the irradiated solutions and theoretically substantiated the thesis that any reaction resulting in formation of aldehydes and HCN would have had to assist in accumulation of  $\alpha$ -amino acids in the hydrosphere of the primitive Earth.

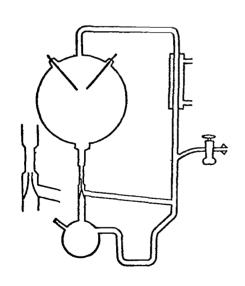


Figure 8. Apparatus for Synthesizing Amino Acids in Electric Discharge (According to S. Miller)

P. Abelson, employing a more complex initial gaseous mixture including CO, CO, and  $N_2$  besides  $CH_4$ ,  $NH_3$ ,  $H_2$ , and  $H_2O$ , derived (Ref. 15) an amino acid mixture similar to Miller's. At the same time he demonstrated that  $\mathrm{NH}_3$  cannot be replaced by  $N_2$ , but that  $CH_4$  can be replaced /81by  ${\rm CO}_2$ . J. Oro, starting with  ${\rm C}_2$ - and  $C_3$ -hydrocarbons and concentrated  $NH_LOH$ , supplemented this list of amino acids synthesized in a spark discharge with leucine, isoleucine, and valine (Ref. 16). Herns, Walter, and Meyer (Ref. 17) introduced hydrogen sulfide into the initial gas mixture, but they were nevertheless unable to synthesize sulfur-containing amino acids -- only thioacetate and thiourea.

K. Grossenbacher (Ref. 18) passed a spark discharge in an instrument which he had specifically designed through a mixture of NH<sub>3</sub>, CH<sub>4</sub>, and H<sub>2</sub> for 100-200

hours, and produced the following mixture of amino acids in an aqueous solution:

(numbers refer to moles) — aspartic acid, 2; threonine, 4; serine, 14; glycine, 16; alanine, 14; lysine, 4; leucine, 2; isoleucine, 2; and glutamic acid, 1. Grossenbacher also detected peptides consisting of glycine and alanine (5:1), as well as of glycine and isoleucine. By the end of the experiment, the polymerization products of amino acids were separated from the solution in the form of minute multi-molecular spheres or droplets. There are fewer investigations of amino-acid synthesis under the action of ionizing radiation on a mixture of primitive gases. We may mention the experiments by K. Dose and B. Rajewsky (Ref. 19), who discovered the formation of acidic and neutral amino acids in the action of x-rays on a gaseous mixture of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O. When Hasselstrom, Henry, and Murr (Ref. 20) irradiated solutions of ammonium acetate with  $\beta$ -rays from a linear accelerator (2 Mev), they obtained glycine and aspartic acid, while Paschke, Chang, and Yaung (Ref. 21), using the  $\gamma$ -radiation of Co<sup>60</sup> (5·10 r) on solid ammonium carbonate, demonstrated the formation of glycine and alanine. Palm and Calvin (Ref. 22) found glycine and aspartic acid when a beam of fast electrons (5 Mev at a dose of  $10^{10}$  ergs) acted upon a mixture of methane, ammonia, hydrogen, and water vapor.

Formation of amino acids during simple heating of initial solutions was first detected by Fox, Johnson, and Vegotsky (Ref. 23). J. Oro et al. (Ref. 24) showed that several amino acids (glycine, alanine, serine, aspartic acid, threonine) are produced simply by heating aqueous solutions of formaldehyde and hydroxylamine for 40-60 hours at 80-100°C, or even at lower temperatures. Similar results were obtained by Lowe, Ress, and Markham (Ref. 25), who heated a 1.5 M aqueous solution of NH<sub>3</sub> and HCN for 18 hours at 90°C, and thereby discovered an appreciable quantity of amino acids, partially included in peptides, and reaction products liberated after hydrolysis (among these, in addition to glycine, alanine, and aspartic acid, they likewise produced leucine, isoleucine, serine, threonine, and glutamic acid).

Harada and Fox (Ref. 26) have recently performed thermal synthesis of amino acids from primitive gases in laboratory experiments imitating volcanic conditions. These experiments are very instructive, and — although the heat of volcanic processes stands in the last place in the above table giving energy sources — this sort of synthesis could have had a certain significance for abiogenic formation of amino acids on the primitive surface of the Earth, since this type of energy was not uniformly distributed over the whole surface, but was local in nature.

Certainly, however, the energy of shortwave ultraviolet rays, which easily reached the terrestrial surface because of the absence of the ozone screen in the preactualistic era, nevertheless was of fundamental significance in the primary abiogenic synthesis of organic substances. The synthesis of amino acids and other organic compounds in experimental imitation of conditions of this sort has now been widely represented in the world literature.

Even W. Groth discovered (Ref. 27) glycine and alanine formation in the action of ultraviolet rays of wavelength 1470 and 1295 Å (resonance lines of the xenon lamp) on a mixture of methane, ammonia, and water vapor. Later, when ethane replaced the methane, he also found  $\alpha$ -aminobutyric acid. A. Terenin for similar purposes used a hydrogen lamp emitting ultraviolet light of wavelength below

1300 Å, in this respect approaching the spectrum of the shortwave radiation of the Sun (Ref. 28). Irradiating a mixture of  $CH_{L}$ ,  $NH_{3}$ , and CO plus water in the liquid state in contact with these gases, Terenin found alamine in the reaction products. Later in Terenin's laboratory, Dodonova and Sidorova established the formation of glycine, alanine,  $\alpha$ -aminobutyric acid, valine, and leucine (or isoleucine) when the same mixtures were irradiated with ultraviolet rays in the 1800-1450 Å region (Ref. 29). Addition of  $H_2S$  or  $GS_2$  to the mixture did not, however, result in formation of sulfur-containing amino acids, which was likewise the case when electrical discharges were employed as the energy sources.

When irradiating aqueous solutions containing 2.5% of formaldehyde and up to 1.5% of ammonium chloride or ammonium nitrate for 20 hours with rays from a PRK-2 lamp, T. Pavlovskaya and A. Pasynskiy (Ref. 14) ascertained that the following amino acids were formed: serine, glycine, glutamic acid, alanine, valine, phenylalanine, and the basic amino acids (leucine, ornithine, and arginine). In the presence of adsorbents (bentonite, kaolinite, limonite, and optical quartz) the same amino acids were found (except the basics) and isoleucine in addition (Ref. 30). Subsequent work demonstrated that threonine was formed, and -- with the formaldehyde replaced by acetaldehyde -- arginine and tyrosine were formed. Similar results have also been produced by numerous other authors by irradiating a mixture of primitive gases and their closest derivatives with shortwave ultraviolet light (Ref. 31). It must be noted that not only do amino acids, but also organic acids and aldehydes, amines and amides, urea in particular, form in the primitive mixtures used for synthesis, both with electrical discharges and with irradiation by ultraviolet rays (Ref. 32).

At the same time, under these conditions polymerization of monomeric molecules occurs, leading to formation of more complex compounds (Ref. 33).

In connection with abiogenic syntheses of amino acids and their polymers, we must briefly touch upon a question which for a long time has been discussed in the literature -- whether primary asymmetrical synthesis is possible. Several theoretical possibilities for this are unfolded by the formation of amino acids under the action of ultraviolet light.

Let us recall that the first asymmetric synthesis was in fact accomplished under laboratory conditions by utilizing the photochemical reaction provoked by the effect of circularly-polarized ultraviolet light (Ref. 34). Together with this, it was demonstrated that light of this sort could also exist under natural terrestrial conditions (Ref. 35). At present, other possibilities for primary formation of asymmetrical compounds outside of living nature are also known. J. Bernal advanced the hypothesis (Ref. 36) that asymmetry could occur in organic substances under abiogenic conditions if synthesis of these substances occurred on the surface of asymmetrical quartz crystals (Figure 9). This assumption was experimentally corroborated in cases of laboratory synthesis performed by A. Terent'yev and Ye. Klabunovskiy (Ref. 37).

G. Wald, however, expresses doubt that any of these abiogenic factors can create conditions for the formation of stable asymmetry (Ref. 38). opinion, geochemical syntheses of organic molecules produced only racemic mixtures, from which individual optical isomers were selected during the formation

/83

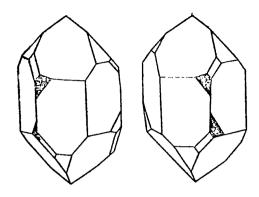


Figure 9. Crystals of Left-Handed and Right-Handed Quartz.

of structures of higher-order -- polypeptides and proteins from amino acids, nucleic acids from nucleotides, and so on. Wald believes, in particular, that /84 this would have had to happen during the selection of protein and polypeptide  $\alpha$ -spirals in the process of formation.

A. Pasynskiy also attributes the greatest importance in solving the problem of the origin of asymmetry to clarification of the formation conditions for stereospecific polymers with an ordered three-dimensional arrangement of the side groups which is achieved in catalysts which are not optically active (Ref. 39). It is possible, he points out, that optical asymmetry did not develop by means of initial formation of optically active monomers and trans-

formation of them into optically active polymers. On the contrary, in the beginning stereospecific polymerization resulted in formation of high-molecular asymmetrical catalysts, and then on the basis of these catalysts, the development of optical asymmetry in low-molecular substances began. Therefore, optical asymmetry is of secondary origin.

Besides the papers on abiogenic synthesis of amino acids and polypeptides, a great number of works have at the present time also been published on the similar synthesis of nucleotide components. J. Oro subjected a mixture of hydrogen cyanide, ammonia, and water to moderate heating (from 30 to 100°C) and synthesized one of the purine bases — adenine (Ref. 40). This experiment demonstrated the possibility of spontaneous formation of such a complex heterocyclic compound from a simple mixture of primitive gases of the Earth's atmosphere, since cyanogen is easily produced from methane when it is irradiated in a water-ammonia system.

Besides adenine among the reaction products, Oro also discovered 4-amino-imidazole-5-carboxamide (AICA), 4-aminoimidazole-5-carboxamidine (AICAI), formamide, and formamidine. Adenine apparently is formed directly from AICAI when it condenses with formamidine (Ref. 41).

Another purine -- guanine -- was synthesized by Oro (Ref. 42) from AICA /85 and urea, which, as was indicated above, is easily formed from primitive gases under ultraviolet irradiation and electric discharges. From the pyrimidine bases, S. Fox synthesized uracil by heating malic acid and urea (Ref. 43). Oro produced uracil from the interaction of urea in an ammonia solution with unsaturated compounds formed from primitive gases in an electric discharge (Ref. 44).

Carbohydrate components of nucleotides -- ribose and 2-deoxyribose -- have been synthesized under conditions like the primitive ones. Ribose was synthesized by Mariani and Torraca (Ref. 45), and 2-deoxyribose was synthesized by

Oro (Ref. 46) by condensing formaldehyde and acetaldehyde in the presence of basic catalysts.

Extensive possibilities for the abiogenic synthesis of nucleotide components have also been demonstrated in the use of ionizing radiation, ultraviolet rays, and electric discharges for this purpose.

According to M. Calvin (Ref. 47), the radioactive emissions of a number of elements, particularly K (which was very abundant in the primitive terrestrial crust), must to a fairly great degree have been important energy sources for cases of abiogenic syntheses. Later on (Ref. 48) Calvin and his collaborators simulated K<sup>40</sup> radiation by subjecting a mixture of primitive gases to electrons of very high energy. Ponnamperuma, Lemmon, Mariner, and Calvin used this procedure to produce adenine from methane, ammonium, and water (Ref. 49). Under these conditions, no guanine, cytosine, uracil, or thymine is formed. It is interesting to compare this fact with the predominant position which adenine occupies in all biological systems; this indicates its great antiquity in the history of the development of life. Molecular orbit computations have indicated that, of all the biologically important purines and pyrimidines, adenine has the greatest resonance energy (Ref. 50) -- which certainly makes its abiogenic synthesis most probable.

From the same mixture -- methane, ammonium, and water -- under the action of ionizing radiation ribose and deoxyribose, and possibly also other sugars, were successfully produced. Sugars are particularly successfully synthesized when the starting mixture contains formaldehyde, which is easily produced from primitive gases with electric discharges. Ribose and deoxyribose were synthesized by Ponnamperuma et al. (Ref. 49) by the action of ultraviolet light or  $\gamma$ -radiation of Co<sup>60</sup> on the gas mixture. With HCN was included in the original gaseous mixture, the use of ultraviolet light led to the synthesis of adenine, guanine, and urea (Ref. 51).

A very important step in the further evolution of organic substances on the /86 road toward the development of life was the abiogenic combination of separate components into nucleotide complexes and the subsequent polymerization of these components into polynucleotides in a fashion similar to that in which amino acids must have polymerized into polypeptides and protein-like substances under the conditions of the primitive terrestrial surface.

A fundamental possibility of such far-reaching abiogenic polymerization of organic substances is confirmed by a number of experiments on models, in which amino acids or compounds related to them were primarily used as the monomers.

We must above all mention the research by S. Akabori (Ref. 52) who, as far back as 1955, indicated the possibility of abiogenic synthesis of protoproteins under conditions of the primitive Earth (i.e., amino acid polymers with random arrangement of the amino acid radicals in the polypeptide chain). He soon proved this possibility experimentally (Ref. 53) by producing amino-acetonitrile (the polycondensate of which was adsorbed on kaoline with formation of polyglycine) from formaldehyde, ammonia, and HCN. It is then possible to introduce side chains into polyglycine by a reaction with aldehydes or with unsaturated

hydrocarbons. In this way, Akabori managed to produce polyglycine and its analogs with a molecular weight of approximately 15,000.

A. Wilson, when conducting experiments like those of Miller (Ref. 54), passed silent discharges through a methane atmosphere over an aqueous solution of yeast sol, ammonia, and hydrogen sulfide in an apparatus which he had especially designed. In this process a polymer film is formed, and under infrared analysis it proves to have structures of the polyethylene type with C-O bonds. This material is hydrophilic and absorbs methylene blue and fuchsin from an aqueous solution. If ammonia and hydrogen sulfide are not employed in the experiment, films of a hydrophobic nature are obtained.

The experiments of S. Fox and his collaborators (Ref. 55) on the thermal polycondensation of a mixture of different amino acids are especially interesting. Here it was shown that at temperatures on the order of 150-180°C, in the presence of considerable amounts of aspartic acid and glutamic acid, there is spontaneous copolymerization of 18 different amino acids leading to the formation of polypeptides with molecular weights from 3000 to 9000. Fox named them proteinoids. Based on color reactions, infrared spectrum, solubility, electrophoretic mobility, and enzymatic attackability, Fox's proteinoids do not differ from such proteins as, for example, casein. They were precipitated out of a 1% aqueous /87 solution of NaCl in the form of globules visible under the microscope (microspheres), which we will examine in greater detail below.

A particular role in primary polymerization processes was apparently played by phosphorus compounds. At temperatures of about 300°C and above, phosphoric acid completely condenses and forms a polyphosphate. Therefore, on the surface of the primitive Earth with its extensive local heating there must have been rather large-scale formation of polyphosphates and their organic compounds.

Inorganic polyphosphates have at present been discovered in significant quantities in lower organisms — in bacteria, algae, fungi, some protozoans, and insects. These are linear polymers of orthophosphoric acid with a molecular weight of 30,000-100,000. Cyclic trimeta— and tetrametaphosphates have also been isolated (Ref. 56) from a number of objects. Inorganic polyphosphates obviously play a substantial role in the metabolism of the lower organisms, in contrast to highly organized living creatures for which they are not characteristic.

On the basis of their research on the green alga Scenedesmus obliquus, I. Kulayev and V. Vagabov (Ref. 57) assume that synthesis of the inorganic polyphosphates detected in them is done completely by phosphorylation which goes on during anaerobic fermentation of glucose, in a similar fashion to this process during storage of energy in ATP\* in alcoholic fermentation or in glycolysis. M. and O. Szymona, on the other hand, synthesized an enzyme from lower organisms which with no help from ATP converts the macroergic phosphate from polyphosphate into glucose with the formation of glucoso-6-phosphate (Ref. 58).

At the Moscow Symposium in 1957, A. Belozerskiy (Ref. 59) already hypothesized that inorganic polyphosphates could play a significant role both in cases

<sup>\*</sup>Translator's Note: ATP designates adenosine triphosphate.

of abiogenic synthesis and in the very first occurring living creatures, replacing ATP to a certain degree.

G. Schramm et al. (Ref. 60) used condensed esterified phosphates in carrying out polycondensation of various biologically important compounds in an anhydrous medium at a temperature on the order of 55-60°C. They obtained polypeptides from alanine-glycineglycine, and from arginine (polyarginine) they obtained polysaccharides of molecular weight 50,000, nucleosides, nucleotides, and, finally, polynucleotides — polyadenine (molecular weight 21,000) and polyuracil (molecular weight 50,000), and so on.

These experiments led G. Schramm to assume that in analogous fashion, owing  $\frac{88}{100}$  to polyphosphates on the surface of the primitive Earth, the formation of protein-like and nuclein-like polymers could occur which, however, must have differed from modern proteins and nucleic acids by more or less random arrangement of the monomer radicals in their chains.

Somewhat later G. Schramm made a more precise determination of the composition of the esterified polyphosphates needed for his syntheses (Ref. 61). This was a mixture of cyclical ethylmetaphosphates and linear ethylpolyphosphates; 70% tetraethyltetrametaphosphate and 30% tetraethyltetrapolyphosphate was required for successful synthesis.

At the Conference on the Origin of Prebiological Systems (Florida, 1963), however, A. Schwartz (Ref. 62) indicated the possibility of synthesis of polynucleotides also by means of free polyphosphoric acid in an anhydrous medium at 60°C, i.e., on a purely inorganic basis.

All of this leads us to believe that in the dawn of life on Earth inorganic polyphosphates were quite able to participate in organization of the simplest mechanisms of joining energy-providing and energy-consuming reactions, but it must be borne in mind that the above-mentioned cases of synthesis were effectuated in an anhydrous medium.

Ponnamperuma, Sagan, and Mariner (Ref. 63) utilized ethylmetaphosphate to synthesize nucleotide components in an aqueous medium. Here the energy source could be ultraviolet light of wavelength 2400-2900 Å, which was perfectly accessible to the primitive terrestrial surface. Syntheses were conducted in aqueous solutions of adenine, adenosine, adenylic acid, ribose, and ethylmetaphosphate. The mixtures were illuminated by ultraviolet light of wavelength 2537 Å at 40°C. In so doing, the authors found transformation of adenine into adenosine, adenosine into adenosinemonophosphoric acid (AMP), AMP into adenosine diphosphate (ADP), and, finally ADP into ATP. Therefore, the feasibility of abiogenic synthesis of adenosinetriphosphoric acid, that basic "energy currency" of living organisms, under conditions of the preactualistic terrestrial surface has been demonstrated.

It may be thought that ethylmetaphosphate was not the sole and earliest source of phosphorus in primitive time. Adenosine may be formed from adenine and ribose under the action of ultraviolet light, not only in the presence of ethylmetaphosphate, but also inorganic phosphoric acid. Ethylmetaphosphoric ether is needed, however, to synthesize adenosinephosphates under the same

conditions.

Eyen more promising results are obtained when ionizing radiation is employed for the same purposes. With this energy source, the synthesis of adenosine in an aqueous solution of adenine and ribose may occur even in the absence of /89 phosphorus, while formation of mono-, di-, and tri-phosphonucleotides requires only the presence of inorganic phosphates in order that it be accomplished (Ref. 64).

In summing up all that has been presented, we see that syntheses using models and effectuated under conditions imitating the chemical and energy environment on the surface of the primitive Earth afford very convincing material for forming an idea of the primary abiogenic transformations of the original carbon compounds in the preactualistic era of our planet's existence.

Those findings which have been obtained from direct observation of the transformation of organic substances under natural conditions both on Earth and on other objects in space are far less significant. Investigations on the transformation of the organic substances in petroleum could be very valuable in this regard, but here abiogenic processes are so intimately interwoven with biogenic ones that it is hard to find our way among them, although recently certain perspectives have been opened up in this direction (Ref. 65).

The same thing may also be said in respect to the evolution of organic substances beyond the confines of our planet. If the initial stages of this evolution, as we saw above, are very universal and may be confirmed on the most varied objects in space, the subsequent transformation of carbon compounds, on the other hand, is far more specific in nature and is closely associated with the developmental characteristics of the given cosmic body. Our research into more complex organic substances, their formation, and their transformation is restricted solely to objects in our own solar system, and only those in the region where planets of the terrestrial type and asteroids were formed.

It is from a study of meteorites, carbonaceous chondrites in particular (Ref. 66), that we derive most of our actual data on the nature and transformations of the more complex extraterrestrial organic substances. Here synthesis of complex organic substances must have proceeded in a reducing atmosphere under conditions of relative cold and of very low gravity. In contrast to the Earth, the carbonaceous chondrites contain water only in the bound state, like hydrated rocks. Organic substances are represented in them chiefly by comparatively high-polymer hydrocarbons.

They were first confirmed as long ago as 1834 by G. Rerzelius (Ref. 67) in the composition of the meteorite Alais\*. A little later, F. Wöhler isolated a certain amount of polymeric hydrocarbon resembling ozocerite from a chondrite /90 which fell near Kaba in Hungary (Ref. 68). Bituminous substances have subsequently been extracted from most of the carbonaceous chondrites now known (Ref. 69).

In our period, for example, G. Mueller has extracted a polymeric organic substance, which he described as asphalt (bitumen), from the meteorite Cold Bokkeveld (Ref. 70). The optical neutrality of this substance enabled Mueller \* Translator's Note: Alais, France. Date of fall: 1806. \*\*Translator's Note: South Africa. Date of fall: 1838.

to conclude that it had been abiogenically produced. It is interesting to note that when the original meteoritic material was treated with boiling hydrofluoric acid, in which ordinarily silicates easily dissolve, that did not take place in this case.

A. Wilson (Ref. 71) sees the reason for this abnormally in the fact that the surface of the silicate particles in the investigated meteor is enveloped with a thin film of organic polymers, like the film which Wilson obtained in his experiments which we described above.

Mass-spectrographic investigations, studies in ultraviolet and infrared light, chromatography, and other modern research methods have made it possible to determine the organic substances in carbonaceous chondrites with precision. The aliphatic nature of the hydrocarbon polymers has been established and their ozocerite-like nature confirmed, as well as the presence of sulfur and oxidizing compounds (Ref. 70). The asphalts in the carbonaceous chondrites Groznaya and Mighei have been examined in the USSR. High-polymer aliphatic hydrocarbons with linear chains of the high-molecular paraffin type were detected in them (Ref. 73).

Nagy, Meinschein, and Hennessy (Ref. 74) subjected the high-temperature distillate from the chondrite Orgueil\* to mass-spectrometric analysis and discovered aliphatic hydrocarbons containing from 15 to 24 atoms of carbon in the chain. These authors even compare them with the fatty acids of natural fats, but the abiogenic formation of this meteoritic organic matter can barely be doubted.

We therefore see that an investigation of meteorities confirms the feasibility of far-reaching complexity and abiogenic polymerization of organic substances, although polymerization in the meteorites took place under somewhat different conditions than on Earth, and therefore resulted only in the formation of comparatively uniform homologous mixtures of polymer hydrocarbons.

The evolution of organic substances on our natural satellite, the Moon, must have proceeded under the very specific conditions stipulated by the lack of an atmosphere and a hydrosphere. From a number of theoretical considerations C. Sagan makes the assumption that the Moon has abiogenic organic matter (Ref. 75). /91 This author believes that this matter could have been formed on the Moon, or must have been brought to its surface by meteorites. It was there exposed to different sorts of transformations resulting from the action of the ultraviolet light and ionizing radiation from which the lunar surface has no protection. Sagan assumes that the organic substances on the Moon are located under a rocky layer shielding them from profound photochemical decomposition at a depth of about 10 meters. Here, according to Sagan, there is a layer of carbon compounds in a concentration of up to 10 grams per square centimeter.

Wilson goes even farther in this respect (Ref. 71), and expresses the supposition that the so-called lunar seas are asphalt lakes formed from abiogenic petroleum which has escaped to the surface of our satellite and then, with the vaporization of its volatile components and under the effect of solar photons, has given rise to asphalt and petroleum coke. For the time being, all of this is, of course, a more or less audacious assumption, and we will have \*Translator's Note: France. Date of fall, 1864.

reliable information at our disposal only when we submit material samplings brought from the Moon to direct analysis.

It was quite recently that great hopes for becoming acquainted with extraterrestrial life were based on a study of the planet nearest us -- Venus. The reason for this was that Venus, which is very favorably located with respect to the Sun, was formed in the same region of the protoplanetary cloud as the Earth, and possesses an almost precisely circular orbit and a mass close to that of the Earth (0.83). It seemed that all this should have stipulated the same course of evolution for carbon compounds as on Earth, but apparently we must now give these hopes up.

Venus has a fairly extensive atmosphere and its surface is hidden from direct telescopic examination from Earth by a thick layer of high clouds. Therefore a study of the conditions on its actual surface was for a long time completely out of our reach, and only the application of radioastronomical methods and the launching of space rockets (Ref. 76) has clarified this matter to a certain extent.

It has been found that the temperature of Venus' surface is very high -- about 300°C, and differs very little between the day and night side of the planet. The atmosphere of Venus lacks a perceptible water-vapor content, and there is apparently no free oxygen or nitrogen at all. Carbon is represented here by carbon dioxide, of which there is about 500 times more than in the Earth's atmosphere. Venus' period of rotation is at least ten Earth days, and the planet perhaps always keeps the same side turned toward the Sun. No significant ionosphere nor magnetic field has been discovered around Venus.

In the light of all these findings, it is very hard to believe that development of life is possible on Venus. The evolution of carbon compounds has obviously traveled completely different paths than on Earth, because of the very dissimilar thermal histories of these planets.

G. Fesenko assumes (Ref. 77) that from the very beginning Venus had no appreciable rotational velocity and was formed without gravitational heating. Since it originally was a comparatively cold body, Venus has not been subjected to internal stratification. The long-lived radioactive elements have remained more or less uniformly distributed in it throughout its whole mass, and have not been brought up to the surface layers because of their affinity to the light silicates, as was the case on Earth. Owing to this, there was no general or local surface heating, crust formation, or separation of a secondary reducing atmosphere abundant in water vapor, methane, ammonia, etc.

Radioactive heat was able to cause only a slow, but gradual warming of the whole planetary mass and has continued until now, determining its present high temperature. Therefore, no magnetic field could form around Venus, nor were any oceanic basins formed on its surface, but the carbon dioxide produced in its bowels accumulated in the atmosphere, since this gas could not be absorbed by silicates and form carbonates.

The study of Mars (Ref. 78) is more promising in the respect in which we are interested, although its mass is substantially less than that of the Earth (0.11 of the Earth's mass) and, because of the planet's great distance from

the Sun, its surface temperature is considerably lower than that of our planet. This temperature undergoes substantial daily fluctuations, varying in the tropic regions from 20°C at noon to -65°C at night. The Martian days are close in length to ours, but its year is notably longer (687 days). The inclination of its equator to the ecliptic is close to the Earth's; therefore, Mars has a change in seasons of the year like ours.

The Martian atmosphere is very greatly attenuated. For the most part, it apparently consists of nitrogen (98%), argon (1.2%), carbon dioxide (0.25%), and a small fraction of water vapor. In the atmosphere of Mars we can detect cirrus clouds of ice crystals and yellow clouds of dust or fine sand. The poles of Mars are covered with white caps consisting of ice in a very thin layer. On the edges of the polar caps and farther toward the equator, in  $\frac{/93}{}$  spring dark greenish-blue contiguous regions are formed which many astronomers regard as vegetation zones gradually expanding as the thawing waters of spring move, but the question of the existence of life on Mars cannot yet be considered as solved.

The low average temperatures, the low quantity of water, and the high irradiation of the Martian surface by ultraviolet light have set up serious barriers against the possibility that the vast majority of terrestrial organisms could live on the surface of Mars. However, many modern authors believe that in the initial periods of its existence Mars was richer in water than it now is; the evolution of organic substances and the rise of life could therefore follow the pattern on Earth. In addition to this, the high capacity of organisms to adapt to environmental conditions make it probable that life, once it developed on Mars, would be able to adapt to the exceptionally severe climate which now exists on this planet.

A fact discovered by W. Sinton (Ref. 79) is therefore very interesting: in the reflected infrared light from Mars, there are three bands -- 3.45, 3.58, and 3.69 microns -- which belong to C-H bonds and indicate the presence of organic molecules, hydrocarbons in particular. These bands characterize only the dark regions of the planet and are lacking in its bright parts. N. Colthup (Ref. 80) interprets these bands as proof of the presence on Mars of organic aldehydes, particularly acetaldehyde, which could have been formed here during the metabolism of anaerobic organisms, in the same way that it is produced at a certain stage in alcoholic fermentation. Sinton also defends the biogenic nature of the organic substances on Mars, since he believes that -- if constant regeneration of these substances (as a result of metabolism) did not occur -- they would then be very rapidly covered with dust or destroyed by ultraviolet light.

In opposition to this, D. Rea (Ref. 81) on the basis of his research considers that Sinton's light bands still cannot be regarded as proof of the presence of life on Mars and that preference must be given to the possibility of an abiogenic formation of organic substances on this planet.

Young, Ponnamperuma, and McCaw (Ref. 82) have recently performed simulation experiments demonstrating the feasibility of abiogenic formation of organic substances and their polymers on Mars. These authors designed a chamber in

which conditions similar to the Martian conditions were created — temperature fluctuating in a daily cycle from -70 to  $+30\,^{\circ}\text{C}$ , pressure of 65 microbars, at  $-\frac{/94}{100}$  mosphere consisting of 65% CO<sub>2</sub> and 33% N (and an addition of 2% acetaldehyde when necessary), soil consisting of limonite and sand, and a small amount of water vapor. The chamber was illuminated by quartz ultraviolet lamps (2537 Å), and the illumination, like the temperature, varied in a daily rhythm.

The experiments showed considerable fixation of CO<sub>2</sub> with formation of organic substances, in particular with the possible formation of acetaldehyde. Acetaldehyde itself under these conditions is easily polymerized, passing into non-volatile compounds, particularly sugars (peptoses and hexoses). The presence of limonite, which adsorbs synthesis products and prevents their re-decomposition by ultraviolet light, is very important.

These authors believe that the organic substances (including acetaldehyde) abiogenically synthesized in the Martian atmosphere gather on the planet's surface and accumulate in its dark areas, while they may be destroyed in the bright regions. This is also an explanation of Sinton's phenomenon. It may be expected that the ever-increasing progress in the conquest of space will soon now enable us to obtain very significant and reliable data on the paths of evolution of organic compounds on the extraterrestrial objects of our solar system.

A specific feature of the conditions under which the abiogenic syntheses of evermore complex organic substances develop on the Earth's surface has been the presence there of an extensive hydrosphere which is totally lacking on the asteroids, the Moon, Venus, and Mars. The particular watery expanses bordering on the atmosphere must have created very favorable conditions for unidirectional evolution of organic substances.

We must bear in mind that in all these cases of synthesis of complex organic substances from primitive gases, which were imitated in the simulation experiments given above, the feasibility of rapidly removing them from the reaction zone in order to avoid destruction of the compounds formed was of very great significance for the quantitative yield of the final reaction products under natural conditions.

D. Hull, for example, is of the opinion (Ref. 83) that ultraviolet light, as the most powerful energy source, was not only able to produce organic substances, but also to destroy them again, and that equilibrium under the conditions of a closed system would have to take a form which did not favor synthesis. Therefore, his calculations show that concentration of organic substances on the surface of the water basins of the Earth could be only negligibly small.

These calculations held true, however, only when the entire process is /95 rigorously restricted merely to a thin surface layer of water and if the synthesized substances cannot leave the reaction zone. Under natural conditions we have no such ideally closed systems, and the products of synthesis necessarily migrate out of the shortwave-radiation sphere of influence. Very favorable conditions in this respect were created by the contact of different reaction zones, e.g., of the water surface absorbing the products of ultraviolet radiation and of the atmosphere; the contact between the cold atmosphere and an electrical

discharge zone; the presence of streams of water and cold gases rapidly removing substances formed on the hot surfaces of volcanic lava, and so on. Of the greatest significance in all these cases is the accumulation of the compounds formed in the waters of seas and oceans which these compounds penetrated from the atmosphere and surface layers of the lithosphere and where they gathered at an appropriate depth, being protected from re-destruction by shortwave radiation. For these reasons, the quantity of organic substances synthesized in the atmosphere and deposited in the waters of the terrestrial hydrosphere must have been very substantial.

According to computations by H. Urey (Ref. 84) and C. Sagan (Ref. 85) in a period of a billion years this quantity must have been approximately 1 kg per  $1 \text{ cm}^3$  of surface, while the concentration of these materials in the waters of the world's oceans would have to reach an order of 1% in the same period.

Therefore, at a certain period in the Earth's existence these waters would have been converted into an unusual "primary broth" containing, along with the inorganic salts, various organic substances — simple and complex monomers and polymers, especially also energy—rich organophosphorous organic compounds capable of entering into numerous interrelationships with each other.

The composition of this "primary broth" was continually changing and evolving, both as a whole and in its separate parts. Its content of organic substances was, on the one hand, continually replenished by endogenic and exogenic sources of carbon compounds (the Earth's crust, meteorites, and comets), while, on the other hand, it was reduced because the organic substances underwent profound decay. Therefore, the concentration of organic substances dissolved in water varied extremely as a whole and, in particular, in the separate, more or less isolated water basins, where it could, for example, rise with local evaporation of the water. Concurrently with these quantitative changes, the qualitative composition of the "primary broth" also evolved, and the substances present in it became more complex and were polymerized, while new compounds arose, particularly in connection with the general changes in conditions on the terrestrial surface.

This may be illustrated by A. Szutka's recent experiments (Ref. 86) on abiogenic synthesis of porphyrins. Based on these experiments, Szutka arrives at the conclusion that porphins and their derivatives must have been produced in the "primary broth" at a relatively late stage in its evolution, at the beginning of the transition period from the preactualistic to the actualistic era when a small quantity of free  $0_2$  appeared in the Earth's atmosphere, and the ozone screen came into being (Ref. 87).

It is interesting to compare this conclusion with research indicating that porphin derivatives take no part in metabolism in several contemporary anaerobes (Ref. 88), while in aerobes they comprise a very important component of the oxidizing enzymes.

Whatever course the evolution of the "primary broth" may have taken, it always remained in principle only a more or less complex solution of inorganic salts and organic substances. The order of the chemical transformations of

organic substances occurring in it, their formation, and their decay differed radically from the sequence which is characteristic of all living beings without exception. In these beings, the sequence of separate reactions is strictly coordinated in the unified process of metabolism because of the specific organization which already pre-exists in them (Ref. 89). Therefore, the order of the processes which are accomplished here is very goal-directed and capable of leading to a constantly recurring synthesis of sometimes very complex and specific compounds, which may thus be produced and be stored in the cell in substantial quantities.

The "primary broth" of course was completely lacking in an order of this sort. Just as in a simple aqueous solution of organic substances, the chemical transformations occurring in the "broth" proceeded in accord only with the general laws of physics and chemistry. They did not have any directed, organized nature, but were effected in all directions in the broadest field of chemical potentialities. Any substance could be altered here in very diverse ways, and individual reactions criss-crossed each other in the most capricious manner. Therefore, a great variety of all sorts of organic substances and their polymers could come into being here, but the more complex and specific a given substance was, the greater the number of sequential reactions that had to participate in its formation, the less probable was its formation, and consequently also the smaller the concentration of this specific substance had to be in the "primary proth."

<u>/97</u>

It is therefore easy to imagine the possibility of extensive abiogenic formation of sugars, amino acids, purine and pyrimidine bases, and their non-specific polymers, but it is extremely improbable that proteins or nucleic acids of the modern type were formed here, i.e., substances assigned a specific, rigorously determined inter- arrangement of amino acid or mononucleotide radicals, with molecular structure, very perfectly adapted to the functions which the protein or nucleic acids support in any living body. For proteins, in particular, this function is the specific catalytic action which enzymes perform in the living cell.

As we saw above, the feasibility of abiogenic synthesis is far from being established for all the amino acids included in the composition of modern proteins. Therefore, it may be assumed that some amino acids arose later under more complex conditions at a higher stage in the evolutionary development of organic matter. If this is so, then the primary polypeptides and protoproteins must not have contained a full complement of amino acids. They were far more primitive polymers than modern proteins, even with respect to their amino-acid composition. Just this alone could restrict their catalytic functions, since such amino acids as, for example, histidine or cystine, are obligatory component parts of the active centers for many modern enzymes.

The strictly-ordered arrangement of amino-acid radicals in the polypeptide chain of modern proteins and the specific packing of this chain in the protein globule, both of which are inherent in modern proteins, are, however, of particularly great significance to the enzymatic activity of these proteins.

This sort of ordered intramolecular structure occurs now only because of the action of very complex highly-organized chemical mechanisms in the living cell, and in the organic matter solution of the "primary broth" its formation is entirely excluded. Therefore, no such highly-organized proteins as the modern ones, particularly enzymes (Ref. 90), which are the unusual organs of the living cell on the molecular level, could form in this broth. Their intramolecular structure is very well and "expediently" adapted to performance of those catalytic functions which they perform in the metabolism of the integral living system. But it is precisely the development of this adaptation under the conditions of a simple aqueous solution in the "primary broth" that is extremely improbable even /98 before the formation there of such integral systems.

The concept of this sort of primitive formation of enzymes is to a certain degree reminiscent of that of the ancient Greek philosopher Empedocles (Ref. 91), who said that the separate organs were originally formed on Earth: "...there grew a multitude of heads without necks, single arms wandered devoid of shoulders, eyes moved without foreheads." Subsequently, these organs ostensibly grew together, and animals and men thus were produced. Today we fully realize that an eye or an arm could come into being only in the evolution of an entire body. By analogy to this, expediently constructed proteins and enzymes could be formed and perfected only in the evolution of an entire system which already possessed a certain -- even though primitive -- metabolism in which enzymes performed their assigned roles. Only in this metabolism-endowed system did the gradual adaptation of the internal structure proceed in the course of evolution -- first of primitive proteins, and then also of enzymes -- toward the functions which they perform in metabolism.

Consequently, the solution of the problem of the primary formation of the ordered and efficient structure of proteins requires first of all an answer to the question of how -- from the chaos of mutually criss-crossing reactions of an aqueous solution -- a definite sequence of metabolism could be organized. We need to clearly represent and experimentally substantiate the method of the possible formation in the "primary broth" of these initial systems, in which the specific order of their interactions with the environment was specified in the evolutionary process, gradually approaching the modern type of metabolism for every living being.

At present, the opinion is widely stated in the scientific literature that these initial systems could be simply individual molecules of those polynucleotides with random arrangement of monomer radicals in the chain, which arose first in the world "broth". Inherent in these molecules was the property of complementarity common to all polynucleotides. Therefore, according to J.B.S. Haldane (Ref. 92), G. Schramm (Ref. 61), and Ponnamperuma et al. (Ref. 63), even under abiogenic conditions the possibility must have been developed for pre-existing nucleotides to synthesize continuously and more rapidly, and for molecules endowed with a certain secondary polymer-chain structure to "multiply automatically" at an ever-accelerating tempo. Subjected to mutations and natural selection, the polynucleotide molecules kept on evolving and improving their secondary /99 structure, approaching in this respect the structure of modern nucleic acids.

On the basis of this evolution "on the molecular level," however, it is difficult to conceive of, not to speak of experimentally reproducing, the origin of metabolism. If this sort of polymerization of mononucleotides is produced in their pure isolated solutions, this leads only to formation of unusual

agglomerations structurally resembling polynucleotides. Under natural conditions this would produce only deposits of these substances similar to deposits of ozocerite or of another mixture of organic homologues. If, however, this polymerization is effected in the presence of other polymers — e.g., polypeptides (which apparently must have taken place in the "primary broth"), — the resultant polynucleotides inevitably form multimolecular complexes with these polymers, and separate out of the surrounding solution as individual systems (coacervate droplets), as has recently been demonstrated in experiments in our laboratory in the Institute of Biochemistry imenii A.N. Bakh of the Academy of Sciences of the USSR (Ref. 94). Here only the size of the polymer molecules formed is of essential significance for this sort of separation, not the order in which the monomer radicals are arranged in their chain; this order may be quite random.

It is important to note that, when complex systems are formed, the equilibrium of the polymerization reaction shifts sharply toward synthesis.

It is precisely these complex systems, not the individual molecules in the solution, which must have been the initial formations which subsequently were organized into primary organisms. Only systems of this sort could evolve on the basis of their interaction with the external environment and of natural selection. They originally included only primitive polypeptides and polynucleotides with no order in their structure. Subsequently, however, the polynucleotides began to acquire a more and more efficient intramolecular structure adapted to the functions which they perform in integral systems which have evolved. Outside of these systems, we cannot conceive of improvement of individual molecules, as we cannot conceive of the formation and perfection of any organ -- eye or arm -- outside of an organism.

The rise of multimolecular complex systems in the originally uniform "broth" of the terrestrial hydrosphere and their subsequent perfection were a further, very important stage in the evolution of carbon compounds on the road toward the development of life.

REFERENCES /100

- 1. Keosian, J. The Origin of Life. Reinhold Pub. Cor., 1964.
- 2. Uffen, R. Nature, 198, 143, 1963.
- 3. Bogorov, V. Dal'niye plavaniya na "Vityaze" (Distant Voyages on the "Hero"). Izdatel'stvo "Znaniya," 1961.
- 4. The Life and Letters of Charles Darwin. Ed. by his son, Francis Darwin, V. 3, p. 18, Murray. London, 1887.
- 5. Oparin, A. Voznikoveniye Zhizni na Zemle (The Rise of Life on Earth), Chapter V, 3rd Ed. Izdatel'stvo Akademii Nauk SSSR, 1957.
- 6. Schorlemmer, C. The Rise and Development of Organic Chemistry (Revised edition). London, 1894.
- 7. Bird, C. Chemical Review, 62, 283, 1962.
- 8. Miller, S., Urey, H. Science, 130, 245, 1959.
- 9. Sbornik: Vozniknoveniye zhizni na Zemle (The Rise of Life on Earth, a Collection). Trudy Mezhdunarodnogo Simpoziuma (Transactions of an International Symposium), August 19-24, 1957, at Moscow. Izdatel'stvo Akademii Nauk SSSR, 1959.

- 10. Proceedings of the Conference on the Origin of Prebiological Systems. Wakulla Springs, Florida, 1963. Ed., S. Fox, Academ. Press, 1965.
- Pavlovskaya, T., Pasynskiy, A. Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry). Izdatel'stvo "Nauka", p. 70, 1964. Pasynskiy, A., Pavlovskaya, T. Uspekhi Khimii, 33, 1198, 1964.
- 12.
- 13. Miller, S. Science, 117, 528, 1953. J. Amer. Chem. Soc., 77, 2351, 1955. In the Collection: Vozniknoveniye zhizni na Zemle (The Rise of Life on Earth), p. 123, 1959. Biochem. Biophys. Acta, 23, 480, 1957.
- Pavlovskaya, T., Pasynskiy, A. In the Collection: Vozniknoveniye zhizni 14. na zemle (The Rise of Life on Earth). Izdatel'stvo Akademii Nauk SSSR, p. 161, 1959.
- 15. Abelson, P. Science, 124, 935, 1956; Cornegie Inst. Wash. Year Book, N. 55, p. 171, 1956; Ann. N. Y. Acad. Sci., 69, 274, 1957.
- Oro, J. Nature, 197, 862, 1963. 16.
- 17. Heyns, K., Walter, W., Meyer, E. Naturwiss., 44, 385, 1957.
- Grossenbacher, K., Knight, C. The Origin of Prebiological Systems. 269. 18. Acad. Press, 1965.
- Dose, K., Rajewsky, B. Biochem. Biophys. Acta, 25, 225, 1957.
- Hasselstrom, T., Henry, M., Murr, B. Science, 125, 350, 1957. 20.
- Paschke, R., Chang, R., Yaung, D. Science, 125, 881, 1957. 21.
- 22. Palm, C., Calvin, M. J. Am. Chem. Soc., 84, 2115, 1962.
- 23. Fox, S., Johnson, J., Vegotsky, A. Science, 124, 923, 1956.
- Oro, J., Kimball, A., Fritz, R., Master, F. Arch. Biochem. and Biophys., 24. 85, 115, 1959; Oro, J., Kamat, S. Nature, 190, 442, 1961.
- 25. Lowe, C., Ress, M., Markham, R. Nature, 199, 219, 1963.
- Harada, K., Fox, S. Nature, 201, 335, 1964; The Origin of Prebiological Systems. Acad. Press, 1965.
- 27. Groth, W. Angew. Chem., 69, 681, 1957; Groth, W., Weyssenhoff, H. der Physik, 4, 69, 1959.
- Terenin, A. In the Collection: Vozniknoveniye zhizni na Zemle (The Rise 28. of Life on Earth). Izdatel'stvo Akademii Nauk SSSR, p. 144, 1959.
- Dodonova, N., Sidorova, A. Biofizika, 6, 149, 1961.
- Pavlovskaya, T., Pasynskiy, A., Grebenikova, A. Doklady Akademii Nauk 30. SSSR, 135, 743, 1960.
- Deschreider, A. Nature, 182, 528, 1958; Cultrera, R., Ferrarri, G. Agro-31. chimica, 5, 108, 1961.
- Grieppe, G., Galotti, M. Gazz. Chim. Ital., 59, 507, 1929; Dodonova, N., 32. Sidorova, A. Biofizika, 7, 31, 1962.
- 33. Ellenbogen, E. E. Abst. Am. Chem. Soc. Meeting, p. 47, Chicago, 1958; Petri, O., Bakhadur, K., Potan, N. Biokhimiya, 27, 708, 1962; Otozai, K., Kume, S., Nagai, S., Jamamoto, T., Fukushima, S. Bull. Chem. Soc. Japan, 27, 476, 1954.

/101

- Kuhn, N., Braun, E. Naturwiss., 17, 227, 1929.
- Byk, A. Z. Phys. Chem., 49, 61, 1904; Naturwiss, 13, 17, 1925. 35.
- Bernal, J. The Physical Basis of Life, London, Routledge, 1951. 36. khimii, 19, 401, 1950.
- Terent'yev, A., Klabunovskiy, Ye. In The Collection: Vozniknoveniye 37. zhizni na Zemle (The Rise of Life on Earth). Izdatel'stvo Akademii Nauk, p. 99, 1959.
- 38. Wald, G. Ann. N. Y. Acad. Scien., 69, 352, 1957; Eyring, G., Jones, L., Spaaks, J. In the Collection: Gorizonty biokhimii (Horizons of

- Biochemistry). Izdatel'stvo "Mir," p. 174, 1964.
- 39. Pasynskiy, A. In the Collection: Vozniknoveniye zhizni na Zemle (The Rise of Life on Earth). Izdatel'stvo Akademii Nauk SSSR, p. 184, 1959.
- 40. Oro, J. Biochem and Biophys. Res. Comm., 2, 407, 1960; Oro, J., Kimball, A. Arch. Biochem. and Biophys., 94, 217, 1961; 96, 293, 1962.
- 41. Oro, J. Nature, 191, 1193, 1961.
- 42. Oro, J. The Origin of Prebiological Systems. Acad. Press, 1965.
- 43. Fox, S., Harada, K. Science, 133, 1923, 1961.
- 44. Oro, J. In the Collection: Problemy evolyutsionnoy i tekhnicheskoy biokhimii (Problems in Evolutional and Technical Biochemistry). Izdatel'stvo "Nauka", p. 63, 1964.
- 45. Mariani, E., Torraca, G. Internat. Sugar. J., 55, 309, 1953.
- 46. Oro, J., A. Fed. Proc. Fed. Amer. Soc. Exptl. Biol., 25, 80, 1962.
- 47. Calvin, M. Chemical Evolution. London Lectures, 1961; Palm, C., Calvin, M. Univer. California Radiat. Lab. Report, Jan. 31, 1961.
- 48. Palm, C., Calvin, M. Submitted to J. Am. Chem. Soc., 1961.
- 49. Ponnamperuma, C., Lemmon, R., Mariner, R., Calvin, M. Proc. Nat. Acad. Sci., USA, 49, 737, 1963.
- 50. Pullman, B., Pullman, A. Nature, 196, 1137, 1962. Molecular Orbitals in Chemistry, Physics and Biology, p. 547. Acad. Press., 1964.
- 51. Ponnamperuma, C. NASA, Jan., 1964.
- 52. Akabori, S. Kagaku (Science in Japan), 25, 54, 1955.
- 53. Akabori, S. In the Collection: Vozniknoveniye zhizni na Zemle (The Rise of Life on Earth). Izdatel'stvo Akademii Nauk SSSR, 1959.
- 54. Wilson, A. Nature, 188, 1007, 1960.
- Fox, S., Harada, K., Vegotskiy, A. Experientia, 15, 81, 1959.
- 56. Kulayev, I. Report at the First All-Union Biochemical Congress in Leningrad, January, 1964, Tezisy (Summaries), No. 1, p. 12. Izdatel'stvo Akademii Nauk SSSR, January, 1964.
- 57. Kulayev, I., Vagabov, V. Biokhimiya, 1965 (in press).
- 58. Szymona, M., Szymona, O. Bull. Acad. Polon. Sci., Ser. Sci. Biol., 9, 371, 1961.
- 59. Belozerskiy, A. In the Collection: Vozniknoveniye zhizni na Zemle (The Rise of Life on Earth). Izdatel'stvo Akademii Nauk SSSR, 1959.
- 60. Schramm, G., Grotsch, H., Pollman, W. Angew. Chem., 74, 53, 1962.
- 61. Schramm, G. Origin of Prebiological System. Acad. Press, 1965.
- 62. Schwartz, A., Bradley, E., Fox, S. Origin of Prebiological System. Acad. Press, 1965.
- 63. Ponnamperuma, C., Sagan, C., Mariner, R. Nature, 199, 222, 1963.
- 64. Ponnamperuma, C. Origin of Prebiological System. Acad. Press, 1965.
- 65. Advances in Organic Geochemistry. Mon. N. 15 Earth Science Series, 1964.
- 66. Krinov, Ye. Osnovy meteoritiki (Rudiments of Meteoritics). Gosteoretizdat, 1955.
- 67. Rerzelius, G. Pogg. Ann., 33, 115, 143, 1834.
- 68. Wohler, F. Strzb. W. Akad., 41, 1859.
- 69. Cohen, E. Meteoritenkunde (Meteorite Knowledge). H. J. Stuttgart, 1894.
- 70. Mueller, G. Geochim. and Cosmochim. Acta, 4, N. 1/2, 1953.
- 71. Wilson, A. Nature, 196, 11, 1962.
- 72. Sztrokay, K., Tolmay, V., Foldvari, M. Vogl. Acte Geologica, 7, 1, 1961.
- 73. Vdovykin, G. Geokhimiya, No. 2, 1962.
- 74. Nagi, B., Meinschein, W., Hennessy, D. Ann. N. Y. Acad. Sci., 93, N. 2,
- \* Translator's Note: Typographical error in original. This should be Nagy.

/102

- 1961; Nature, 189, 967, 1961.
- 75. Sagan, C. Organic Matter and the Moon. National Research houncil Pub., 757, 1961.
- 76. Yames, J. Scientific American, July, 70, 1963.
- Fesenkov, G. In The Collection: Problemy evolyutsionnoy i tekhnicheskov 77. biokhimii (Problems in Evolutional and Technical Biochemistry), p. 5,
- 78. Martynov, D. In the Collection: Vozniknoveniye zhizni vo Vselennoy (The Rise of Life in the Universe). Izdatel'stvo Akademii Nauk SSSR, p. 56, 1963.
- Sinton, W. Science, 130, 1234, 1959. 79.
- Colthup, N. Science, 134, 529, 1961.
- Rea, D. Nature, 200, 114, 1963; R la, D., Belsky, T., Calvin, M. Science, 81. 141, 923, 1963.
- Young, R., Ponnamperuma, C., McCaw, B. Reports at the COSPAR Conference 82. (Manuscript). Florence, 1964.
- Hull, D. Nature, 186, 692, 1960. 83.
- 84. The Planets: Their Origin and Development. Yale Univ. Press, Urey, H. 1952.
- Sagan, C. Rad. Research, 15, 174, 1961. 85.
- Szutka, A., Hazel, J., McNabb, W. Rad. Research, 5, 597, 1959; Szutka, A. 86. Rad. Research, 19, 183, 1963. The Origin of Prebiological System. Acad. Press, 1965.
- 87. Krasnovskiy, A., Umrikhina, A. Doklady Akademii Nauk SSSR, 155, 691, 1964.
- Dolin, M. The Bacteria, V. 11, p. 425, Acad. Press, 1961; Oparin, A., 88. Kharat'yan, Ye., Gel'man, N. Doklady Akademii Nauk, 157, 207, 1964.
- 89. Hinshelwood, C. The Chemical Kinetics of the Bacterial Cell, Clarendon Press, Oxford, 1947; J. Chem. Soc., p. 745, 1952.
- 90. Dickson, M., Webb, E. Enzymes. Izdatel'stvo Inostrannoy Literatury, 1963.
- 91. Simplicius on Aristoli's. De Caelo, 586, 29; Diels, H. Die Fragmente der Vorsokratiker (Fragments of the Pre-Socratics). Ed. 2, V. 1, p. 190. Empedokles, 1357). Berlin, 1906.
- 92. Haldane, J. Origin of Prebiological Systems. Acad. Press, 1965.
- 93. Pattee, H. Biophysical J., 1, 683, 1961; Vanyushin, B. Priroda, p. 29, April, 1963.
- Oparin, A., Serebrovskaya, K. Doklady Akademii Nauk SSSR, 148, 943, 1963. 94.

## IV. THE RISE OF PREBIOLOGICAL SYSTEMS

/103

It is characteristic of life that it is not simply scattered in space, but is represented by individual, very complex systems -- organisms -- which are separated from the external world. Their rise could occur only on the basis of prolonged evolution, the gradual perfecting of some far more simple initial systems which had separated themselves from the over-all uniform solution of organic substances (Ref. 1).

In the beginning these systems could even have been simply sections of the "primary broth" which had isolated themselves, were separated from the medium surrounding them by some dividing surfaces, but were capable of interacting with this medium.

Goldacre's vesicles (Ref. 2) may be cited to illustrate such a system which forms even under present-day conditions in nature (Figure 10). Goldacre has recently described the formation of small closed bubbles contained in a protein-lipid envelope on the surface of natural bodies of water. They are generated from the protein-lipoid film on the water's surface simply under the action of wind. This film is formed today from the products of bodily decay of organisms, but the simulation experiments of Wilson (Ref. 3) show that it could also have been generated from abiogenic carbon compounds in the primitive ocean.

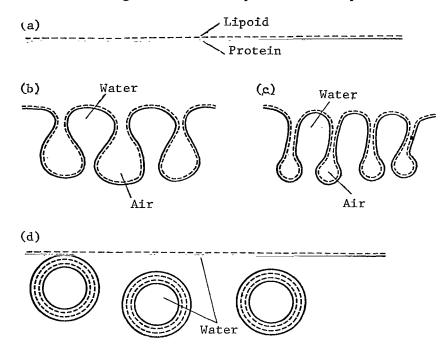


Figure 10. Vesicle Formation (According to R. Goldacre). a, b, c, d  $-\!\!\!-\!\!\!-$  Successive Stages.

As pointed out above, Fox et al. (Ref. 4), simulating volcanic conditions, /104 subjected a mixture of 18 amino acids (with dicarbonic acids in the majority) to heating at 170°C in a piece of lava. This produced polymers — proteinoids which in aqueous solutions formed multimolecular microspheres 2-7µ in diameter with an external resemblance to the regular elements that have been detected in meteorites (Figure 11). The artificially produced proteinoid microspheres can keep their shape for a protracted period and withstand centrifuging at 3000 rpm. They are resistant to the operations accompanying the preparation of microtomic slices, as was first demonstrated by R. Young and E. Munoz (Ref. 5), are Gram-positive, and display a number of other characteristics connecting them with bacteria cells (Ref. 6). The electron-microphotographs shown at the Wakulla Springs Conference (1963) by S. Fox and R. Young (Ref. 7) are indeed striking in their resemblance to similar photographs made of bacteria slices. These microphotos displayed the /105 granular structure of the microspheres and even the double membrane coating the



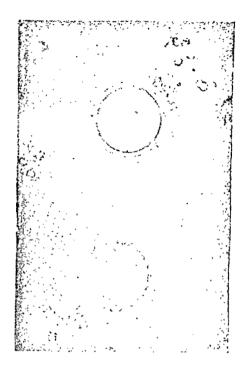


Figure 11. Simple Microspheres of S. Fox Under the Optical Microscope (size -- 7 microns)

Figure 12. The Same Microspheres as in Figure 11 Under the Electron Microscope. Note the Double Membrane.

surface of these artificial products like the protein-lipoid membrane of a living cell (Figure 12).

All this demonstrates the remarkable capacity for three-dimensional self-organization belonging to macro-molecular complexes formed under conditions resembling primitive ones, and must be taken into account when studying the problem of the formation of the protoplasmic structure of primitive organisms.

We must always, however, think of any system as being organized not only in space, but also in time, since these two aspects of organization are inseparable from each other. Any system possesses, on the one hand, a certain size and structure — the patterned arrangement of its parts with respect to each other — and, on the other hand, a definite combination and sequence to the processes which take place within it. In protoplasm, this last form of organization — the metabolism continuously going on in it — is of particularly great significance, because even the very structure of protoplasm is not by nature static, but dynamic. Its stability comes not from unchangeability, but, on the contrary, from the continuous nature of the biochemical processes going on in the protoplasm, the patterned combination of synthesis and breakdown (Ref. 8).

The comparatively simple, abiogenic formations which in the past took shape from the organic materials of the original ocean, and which were the first systems on the way toward the development of life, had to evolve both in respect to spatial organization involving complexity and improvement of the structure, and with respect to temporal organization in order to establish a definite sequence in the processes occurring in these formations.

For an investigator working on the problem of the development of life, it is therefore exceptionally important to ascertain the evolutionary ways in which the definite order of metabolism arose from the chaos of the orderless, mutually criss-crossing reactions in the "primary broth." The solution to this exceptionally complex problem must be approached from two sides. On the one hand, profound comparative biochemical research on modern organisms is necessary to enable us to bring to light the reactions and combinations thereof which underlie metabolism in all living creatures without exception and which may hence be regarded as the oldest, original metabolic systems that had come into existence even when the tree of life had not ramified into its individual branches.

The other path of research is to set up experiments on models which in  $\frac{106}{100}$  some measure reproduce the phenomena that occurred under the conditions of the "primary broth." The aim of these experiments is to demonstrate the possibility (or even the impossibility) that under these conditions any individual systems could arise whose evolutionary development would gradually organize the set of reactions occurring in these systems, consistently approximating the order which is inherent in even the most primitive metabolism.

In this respect, Fox's microspheres in the form in which they are produced under thermal action open up no great possibilities. Their structure is static. This is very favorable for electron-microscopic studies of them, but it creates great difficulties for their transformation into dynamic systems which might be used in simulating the evolution of metabolism.

A characteristic feature of biological polymers — proteins, nucleic acids, carbohydrate and lipoid polymers — is their clearly pronounced capacity to form complexes with other high-molecular organic substances. In this process, /107 structures frequently occur whose physical and chemical properties substantially differ from those of the individual substances comprising them.

Bungenberg de Yong mixed dilute aqueous solutions of gelatin and gum arabic together and observed (Ref. 9) that, under certain temperature and acidity conditions rather common in nature, the mixture becomes very turbid. The reason for this is that the molecules of gelatin and gum arabic, which were previously uniformly distributed throughout the whole volume of the diluent, begin to join together into unbroken molecular "swarms" or "clusters." When these clusters reach a certain rather large size, they separate from solution in the form of droplets visible under the ordinary optical microscope and swim freely in the water surrounding them, which now proves to be already almost entirely deprived of these polymers (Figure 13).

Bungenberg de Yong called the structures which he produced 'coacervate droplets' (Ref. 10). He showed (Ref. 11) that the coacervation process is one /108

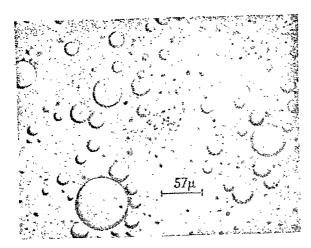


Figure 13. Coacervate Droplets of Gelatin and Gum Arabic

of the most powerful methods of concentrating high-polymer substances from greatly attenuated solutions of them. Coacervate droplets were, for example, thus separated from a solution containing only 0.001% of gelatin. In the droplets themselves, however, the polymer concentration reaches several tens of percents. Although the droplets are liquid in consistency and in several cases are hydrophilic, they are distinctly separated from the aqueous solution surrounding them (the so-called equilibrium liquid) by an abrupt surface boundary, although they are able to interact chemically with their environment. Both Bungenberg de Yong himself (Ref. 12) and subsequent authors (Ref. 13) produced coacervate droplets from many other organic polymers besides gelatin and gum arabic. To be more specific in our laboratory

in the A.N. Bakh Institute of Biochemistry, K. Serebrovskaya (Ref. 14) produced 17 types of coacervates of differing composition whose drops included various proteins (including albumin and histone), nucleic acids, polyglycosides, lipoids, chlorophyll, etc. (Figure 14).

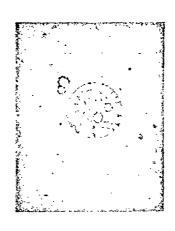


Figure 14. Nucleoproteide Coacervate, RNA + Histone, pH 9, X 800

In all these cases, the substances used were of biogenic origin and were isolated from living organisms. This, of course, was done because that is the simplest way to produce the necessary polymers under laboratory conditions, but for this reason the opinion has even been expressed in the literature that only substances of biological origin, with their regularly constructed secondary and tertiary structure, can form coacervate droplets (Ref. 15). We were able to refute this opinion by experiment, and /109 to demonstrate that the decisive role in the coacervation process is played only by the degree of polymerization of the substances combined in the droplet, and not any particular regular order of the monomers in their polymer chain (Ref. 16). To do this, we synthesized polyadenine in vitro from adenosine

diphosphate in an aqueous medium in the presence of or with the parallel formation of another polymer (e.g., polysine) (Figure 15). Not only was a definite degree of polymerization of the substance to be synthesized achieved, but coacervate droplets containing these polymers were separated from solution. The

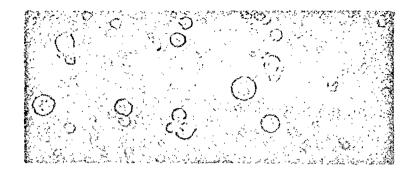


Figure 15. Coacervate Droplets Which Appeared During Synthesis of Polyadenine in the Presence of Histone

/110

coacervate droplets, therefore, are formed not merely when solutions of natural proteins, nucleic acids, and other biogenic substances are mixed, but also when solutions of artificial polymers with monotonous chain structure or with no complex regular secondary structure are mixed. A similar precipitation of coacervate droplets must also have occurred under the conditions of the "primary broth," where non-specific polymerization of different organic substances, particularly amino acids and mononucleotides, occurred. At the same time, the coacervate droplets are the sort of individual multimolecular systems whose stability is dynamic, based on the continuous interaction of these formations with their environment like open systems. Therefore, coacervate droplets are very convenient models for reproducing under laboratory conditions the possible paths traveled by the formation both of the structure and the metabolism in the original systems during the development of life (Ref. 17).

Coacervate droplets may be obtained from two or more components. Droplet size and concentration of polymers contained in them depend chiefly on the character of the substances comprising them, but even droplets of the same composition can vary greatly in volume and weight. Below we give a table (Table 6) which we have borrowed from the work of T. Yevreinova (Ref. 18) and which describes the volume and weight of the droplets, the polymer concentration in individual droplets (C), and the relationship of this concentration to that of the same substances in the surrounding diluent.

Table 6 shows that coacervation involves polymer concentration in the drop-lets which is many tens of times, sometimes even hundreds of times, greater than their concentration in the solution. Droplets of the very same composition may differ greatly in degree of polymer concentration in them, but the smaller a given individual droplet is in volume, the higher the concentration generally of the substances it contains and the lower the hydration of these substances in the droplet.

Employing interference microscopy, Yevreinova found a considerable fluctuation in concentration of the substances not merely in individual droplets of the very same composition, but even within the confines of the very same droplet

	<del></del> -	1	1						
Number in	Diameter,	Volume 10-12 cc	Weight 10-12 gram	Concentration (C), %	(C) Droplet				
0rder	TO CIII		10 81	(9), "	(C) Solutions				
1	2	3	4	5	6				
		PROT	' FEIN + CARBOHYI	DRATE					
			lbumin + Gum (p						
1	3.08	15.3	5.2	34	50				
2	3.30	18.8	6.0	32	47				
3	6.16	122	12.9	21	31				
•	Histone + Gum (pH 5.5-6)								
4	3.30	18.8 122.1	9.7 53	52 43	94 79				
5 6	6.16 8.36	305.3	102.3	38	61				
·		•	n Protamine + G	Gum (pH 6.0)					
7	4.40	44.6	13.8	31	30				
8	4.62	51.5	15.5	30	37				
9	8.69	342	82	24	30				
,			otamine + Gum	_					
10 11	3.52 6.27	22.8 127.9	11.3 44.1	50 34	33 23				
12	7.48	218.6	63.4	29	19				
·		Clupei	ne + Gum (pH 6	.0-6.5)					
13	1.98	4.1	1.5	36	37				
14	3.19	16.8	5.4	32	33				
15	6.27	128.2	35.9	28	29				
			ROTEIN + PROTE						
			erum Albumin (						
16	2.20	5.6 32.4	2.4	44 35	44 35				
17 18	3.96 5.50	86.9	11.3 15.6	18	18				
Histone + Gelatin (pH 6.2-7.3)									
19	4.18	38.2	13.5	35	60				
20	5.50	86.9	25.7	30	50				
21	11.66	762.2	107.2	15	25				
_	Clupeine + Gelatin (pH 8.6-8.8)								
22	3.30	18.8	2.6	14	13 10				
23 24	5.61 7.92	91.8 259.6	10.1 20.8	11 8	7				
,		•	•						

Number in 10-4 cm 10-12 cc					·	/				
PROTEIN + NUCLEIC ACIDS   Clupeine + RNA (pH 8.0-8.6)		Diameter,								
PROTEIN + NUCLEIC ACIDS  Clupeine + RNA (pH 8.0-8.6)  25    1.98		10 <sup>-4</sup> cm	10 <sup>-12</sup> cc	10-12 gram	(C), %	(C) Solutions				
Clupeine + RNA (pH 8.0-8.6)  25	1	2	3	4	5	6				
Clupeine + RNA (pH 8.0-8.6)  25	PROTEIN + NUCLEIC ACIDS									
26   4.84   59.3   26.0   44   258   179    Clupeine + DNA (pH 7.6-8.2)  28   1.76   2.8   2.3   56   431   85    29   4.04   35.3   9.1   26   185   30   9.24   412.9   56.2   14   85    Histone + RNA (pH 7.0-7.6)  31   1.76   2.8   1.5   58   116   32   4.18   38.3   5.6   15   29   33   15.84   2080.1   100   4   8    Histone + DNA (pH 6.8-7.6)  34   2.2   5.6   2.3   42   84   35   4.4   44.6   11.4   25   51   36   16.72   2446.5   169   7   14    Protein + Carbohydrate + Nucleic Acid  Gelatin + Gum + DNA (pH 3.8-4.0)  37   2.32   6.5   2.4   37   55   38   5.35   79.4   19.8   25   37   39   6.43   137.90   31.6   23   34    Gelatin + Gum + DNA (pH 3.8-4.0)  40   34.5   21,400   4,800   22   33   41   41.4   37,100   5,800   16   23   42   62.1   125,100   12,800   10   15    Gelatin + Gum + RNA (pH 3.8-4)  43   34.5   21,400   42,800   20   30   44   53.8   81,300   11,200   14   21   45   179.4   3016,800   235,010   8   11    Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12   47   85.1   322,000   19,900   6   9										
26   4.84   59.3   26.0   44   258   179    Clupeine + DNA (pH 7.6-8.2)  28   1.76   2.8   2.3   56   431   85    29   4.04   35.3   9.1   26   185   30   9.24   412.9   56.2   14   85    Histone + RNA (pH 7.0-7.6)  31   1.76   2.8   1.5   58   116   32   4.18   38.3   5.6   15   29   33   15.84   2080.1   100   4   8    Histone + DNA (pH 6.8-7.6)  34   2.2   5.6   2.3   42   84   35   4.4   44.6   11.4   25   51   36   16.72   2446.5   169   7   14    Protein + Carbohydrate + Nucleic Acid  Gelatin + Gum + DNA (pH 3.8-4.0)  37   2.32   6.5   2.4   37   55   38   5.35   79.4   19.8   25   37   39   6.43   137.90   31.6   23   34    Gelatin + Gum + DNA (pH 3.8-4.0)  40   34.5   21,400   4,800   22   33   41   41.4   37,100   5,800   16   23   42   62.1   125,100   12,800   10   15    Gelatin + Gum + RNA (pH 3.8-4)  43   34.5   21,400   42,800   20   30   44   53.8   81,300   11,200   14   21   45   179.4   3016,800   235,010   8   11    Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12   47   85.1   322,000   19,900   6   9	25	1.98	4.1	2.4	59	348				
Clupeine + DNA (pH 7.6-8.2)  28	26	4.84	59.3	26.0	44	258				
28	27	7.15	•			179				
29   4.04   35.3   9.1   26   185    Histone + RNA (pH 7.0-7.6)  31   1.76   2.8   1.5   58   116   32   4.18   38.3   5.6   15   29   33   15.84   2080.1   100   4   8    Histone + DNA (pH 6.8-7.6)  34   2.2   5.6   2.3   42   84   35   4.4   44.6   11.4   25   51   36   16.72   2446.5   169   7   14    Protein + Carbohydrate + Nucleic Acid  Gelatin + Gum + DNA (pH 3.8-4.0)  37   2.32   6.5   2.4   37   55   38   5.35   79.4   19.8   25   37   39   6.43   137.90   31.6   23   34    Gelatin + Gum + DNA (pH 3.8-4.0)  40   34.5   21,400   4,800   22   33   41   41.4   37,100   5,800   16   23   42   62.1   125,100   12,800   10   15    Gelatin + Gum + RNA (pH 3.8-4)  43   34.5   21,400   42,800   20   30   44   53.8   81,300   11,200   14   21   45   179.4   3016,800   235,010   8   11    Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12   47   85.1   322,000   19,900   6   9										
14		1	3	) 1		`				
31										
32   4.18   38.3   5.6   15   29   8    Histone + DNA (pH 6.8-7.6)  34   2.2   5.6   2.3   42   84   35   4.4   44.6   11.4   25   51   36   16.72   2446.5   169   7   14    Protein + Carbohydrate + Nucleic Acid  Gelatin + Gum + DNA (pH 3.8-4.0)  37   2.32   6.5   2.4   37   55   38   5.35   79.4   19.8   25   37   39   6.43   137.90   31.6   23   34    Gelatin + Gum + DNA (pH 3.8-4.0)  40   34.5   21,400   4,800   22   33   41   41.4   37,100   5,800   16   23   42   62.1   125,100   12,800   10   15    Gelatin + Gum + RNA (pH 3.8-4)  43   34.5   21,400   42,800   20   30   44   53.8   81,300   21,200   14   21   45   179.4   3016,800   235,010   8   11    Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12   47   85.1   322,000   19,900   6   9										
15.84   2080.1   100   4   8				1						
Histone + DNA (pH 6.8-7.6)  34			l l	1	1					
34   2.2   5.6   2.3   42   84 35   4.4   44.6   11.4   25   51 36   16.72   2446.5   169   7   14 Protein + Carbohydrate + Nucleic Acid  Gelatin + Gum + DNA (pH 3.8-4.0)  37   2.32   6.5   2.4   37   55 38   5.35   79.4   19.8   25   37 39   6.43   137.90   31.6   23   34 Gelatin + Gum + DNA (pH 3.8-4.0)  40   34.5   21,400   4,800   22   33 41   41.4   37,100   5,800   16   23 42   62.1   125,100   12,800   10   15 Gelatin + Gum + RNA (pH 3.8-4)  43   34.5   21,400   42,800   20   30 44   53.8   81,300   11,200   14   21 45   179.4   3016,800   235,010   8   11 Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12 47   85.1   322,000   19,900   6   9	33	13.04	•	•	•	1 0				
35    4.4	34	1 2 2		_		l 84				
Protein + Carbohydrate + Nucleic Acid  Gelatin + Gum + DNA (pH 3.8-4.0)  37			44.6			N				
Gelatin + Gum + DNA (pH 3.8-4.0)  37	36	16.72	2446.5	169	7	14				
37   2.32   6.5   2.4   37   55   38   5.35   79.4   19.8   25   37   39   6.43   137.90   31.6   23   34				-						
38   5.35   79.4   19.8   25   37   34   Gelatin + Gum + DNA (pH 3.8-4.0)  40   34.5   21,400   4,800   22   33   34   41   41.4   37,100   5,800   16   23   42   62.1   125,100   12,800   10   15   Gelatin + Gum + RNA (pH 3.8-4)  43   34.5   21,400   42,800   20   30   30   44   53.8   81,300   11,200   14   21   45   179.4   3016,800   235,010   8   11   Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12   47   85.1   322,000   19,900   6   9		•								
39   6.43   137.90   31.6   23   34    Gelatin + Gum + DNA (pH 3.8-4.0)  40   34.5   21,400   4,800   22   33   41   41.4   37,100   5,800   16   23   42   62.1   125,100   12,800   10   15    Gelatin + Gum + RNA (pH 3.8-4)  43   34.5   21,400   42,800   20   30   44   53.8   81,300   11,200   14   21   45   179.4   3016,800   235,010   8   11    Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12   47   85.1   322,000   19,900   6   9										
40   34.5   21,400   4,800   22   33   34   41.4   37,100   5,800   16   23   23   42   62.1   125,100   12,800   10   15			1							
41		•	•	•	•	•				
42   62.1   125,100   12,800   10   15  Gelatin + Gum + RNA (pH 3.8-4)  43   34.5   21,400   42,800   20   30  44   53.8   81,300   11,200   14   21  45   179.4   3016,800   235,010   8   11  Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12  47   85.1   322,000   19,900   6   9		34.5								
Gelatin + Gum + RNA (pH 3.8-4)  43		1								
43   34.5   21,400   42,800   20   30   344   53.8   81,300   11,200   14   21   3016,800   235,010   8   11   3016,800   11,200	42	02.1	•		•	[ 13				
44   53.8   81,300   11,200   14   21   21   45   179.4   3016,800   235,010   8   11   11   12   13   14   14   15   15   15   15   15   15	4.2	۱ ۵۸ ۵				1 30				
45   179.4   3016,800   235,010   8   11  Protein + Carbohydrate + RNA  46   29.9   14,000   1,200   8   12  47   85.1   322,000   19,900   6   9					•					
46     29.9     14,000     1,200     8     12       47     85.1     322,000     19,900     6     9		3		1						
47 85.1 322,000 19,900 6 9	Protein + Carbohydrate + RNA									
					P .					

				•				
Number in Order	Diameter, 10 <sup>-4</sup> cm	Volume 10-12 cc	Weight 10 <sup>-12</sup> gram	Concentration (C), %	(C) Droplet (C) Solutions			
1	2	3	4	5	6			
			PROTEIN + LIPI	ID	•			
	Gelatine + Oleate (pH 8.4-8.6)							
49 50 51	7.7 17.78 24.36	238.9 2941.8 7567.9	55 505.4 1190.2	28 17 16	3.6 2.7 2.4			
		MULTI	COMPONENT COAC	CERVATE				
	Phosphory	Lase + Histo	one + Starch +	Gum, Etc. (pH 6.	0-6.2)			
52 53 54	2.41 4.18 5.50	7.4 38.2 86.9	3.7 14.2 24.1	50 37 28	75 55 41			

(Figure 16), (Ref. 19). The droplet may contain vacuoles where polymer concentration is very reduced. On the contrary, in other instances there may be a certain structured nature in the separate regions of the droplet. The presence of such a structure is indicated by the shape of certain coacervate formations, which is not always spherical.

Under the ordinary optical microscope, it is rather difficult to detect any particular structure in coacervate droplets, but this structure becomes apparent to a certain degree when the droplets (without being preliminarily dried) are photographed under an electron microscope provided with the gas microchamber of I. Stoyanova (Ref. 20) (Figure 17).

The lack of uniformity in distribution of the substances in the droplets becomes apparent with particular clarity when one of the components is a nucleic acid and the other is histone. Nucleic acid concentration in the individual structural formations of the coacervate droplets has been measured by T. Yevreinova (Ref. 21) using an MUF-4 ultraviolet microscope (Figure 18). Here it was demonstrated that this concentration may fluctuate within very wide limits, revealing individual features of separate droplets even when the latter have been produced in the same solution. According to findings of Bungenberg de Yong (Ref. 22) and several other authors (Ref. 23), a film-like structure may appear on the coacervate droplet surface in the presence of lipoids, but even when this film is absent there is always a distinct boundary between the droplet and the medium surrounding it. The droplets are nonetheless not isolated from this medium, but possess the capacity of interacting with it, which is very important for their further evolution.

This interaction is expressed chiefly in the capacity of the droplets to selectively absorb materials from the external medium (the equilibrium liquid).

It is particularly easy to demonstrate this capacity by adding various dyes to the equilibrium liquid. We can observe directly under the microscope the manner in which the stain is gradually concentrated in the droplets, while the surrounding solution correspondingly loses color. T. Yevreinova's measurements showed that such dyes as neutral red, methylene blue, etc. collect in the droplets (e.g., those of gelatin and gum arabic) in quantities exceeding many tens of times their initial concentration in the original solution. T. Yevreinova et al. (Ref. 24) have also established the selective concentration of amino acids in the coacervate droplets, but for some of them (e.g., tyrosine) it is hundreds of times greater than in the surrounding solution, while for others (e.g., tryptophan) it is only twice as great. In contrast to this, sugars and mononucleotides distribute themselves uniformly between the droplets and the surrounding solution, so that equal volumes of droplets and solution contain the same amount of these substances. Of course, the capacity to concentrate the various compounds and the degree of this concentration change very greatly as droplet composition and structure vary.

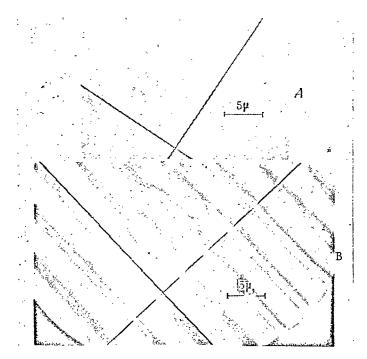


Figure 16. (A) - Coacervate Droplets with Vacuole, (B) - the Same Droplet Under the Interference Microscope.

The ability to concentrate substances from the surrounding solution still /115 does not, however, make the coacervate droplet the model of a living system. Equilibrium sets in very quickly between the droplet and the solution around it, and the droplet assumes a thermodynamically stable state -- it becomes a static system. In contrast to this, any cell or multicellular organism is in a state of continuous interaction with its external environment during its lifetime.

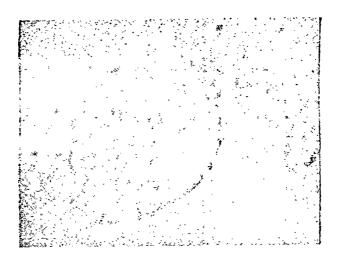


Figure 17. Coacervate Droplet of Serum Albumin + Gum + RNA + RNAase, X 1200. Electron Microscope Gas Chamber.

A living system exists only while the numerous biochemical processes which constitute metabolism occur uninterruptedly in it and with great rapidity. As soon as these processes stop or radically change, the protoplasmic system itself is destroyed with constant motion, not with inalterability or quiescence. plasm is therefore not a static, but a continuous system (Ref. 25).

That great dialectician of Ancient Greece, Heraclitus, in his time noted this characteristic feature of living beings when he taught that our bodies flow like rivers, and the matter in them is renewed like the water in a stream (Ref. 26). It is, indeed, a stream, or simply a flow of water gushing from a faucet, which enables us to understand in the simplest manner a number of the most essential features of the organization of such irreversible or open systems as the living protoplasm, in particular. If the faucet is opened gently and the pressure in the plumbing system remains constant all the time, then the stream of water flowing out keeps its external appearance almost unchanged, its shape /116 is figuratively frozen. But we know that this shape is merely the visible expression of a continuous stream of water particles which are gradually entering and leaving it at a certain rate. The very existence of this system involves the continual and uniform passage of constantly new molecules of water in this stream. If we stop that process, the stream itself disappears as a definite system.

Analogously, the organization of protoplasm is also based on a certain continuous state which comes into being because the living organism is involved in a constant interchange of substances and energy with its environment, because within it there is a series of irreversible, conjunct processes occuring at a constant rate. This results in the fact that the substances coming in from the

outside environment are subjected to a number of transformations in the organism,

while their decomposition products are again excreted into the external medium.

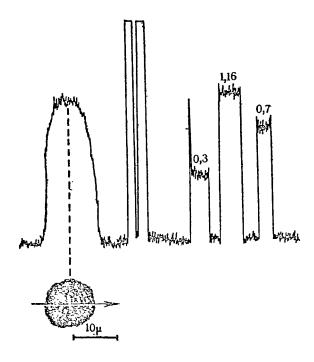


Figure 18. Quantitative Determination of Nucleic Acids in the Coacervate Droplet (Clupeine + DNA), MUF-4\*.

The employment of tagged atoms in biochemical and physiological research (Ref. 27) has shown beyond doubt that all the substances of the living body — its proteins, nucleic acids, lipoids, etc. — are entirely renewed in very short periods of time and that the material substrate of life is continuously being /117 exchanged with the environment, continuously breaking down, and being built up anew from the materials of the external world. Thus, the principle of the unity of the organism and the environment, the thesis that a living being cannot be considered apart from its environment, outside of this unity, has been completely confirmed.

I. Prigogine in his interesting book <u>Introduction to the Thermodynamics of Irreversible Processes</u> (Ref. 28) divides all organic systems into the following basic groups: open, closed, and isolated. The open group contains systems in which there is a constant interchange both of matter and of energy with their environment. In closed systems, this exchange is restricted to energy, and exchange of matter is lacking. The isolated group of systems includes those completely insulated from their external environment, exchanging neither matter nor energy with it. The last two groups of systems may be combined under the general

<sup>\*</sup> This refers to an ultraviolet microscope.

term 'closed' by contrasting them with open systems, to which, in particular, living organisms belong.

In closed systems, only those substances contained in the system can enter into chemical reaction. The constancy of the system's properties in time is characterized by an equilibrium state in which the rate of the reaction proceeding in one direction equals the rate of the inverse reaction. The thermodynamic criterion of this equilibrium is the minimum free energy of the system and the maximum value of its entropy (in other words, its transfer into the most probable of all the possible states). The processes which go on spontaneously in the closed system cannot transfer it to a less probable state -- i.e., they can only keep system entropy constant or increase it, depending on whether we are dealing with reversible or irreversible processes. When system entropy grows, equilibrium is absent, and, on the contrary, when equilibrium sets in, the entropy growth rate is zero. On the other hand, in an open system substances are continuously coming from the external medium into a system which is somehow separated from this medium, and the chemical compounds produced in this system are continually being returned to the medium. Therefore, the constancy of an open system's properties in time is characterized not by thermodynamic equilibrium (as is observed in closed systems), but by the onset of a continuous state, in which the chemical changes proceeding in one direction and substance diffusion in the system are maintained at a constant rate.

Thermodynamic equilibrium and the continuous state resemble each other in /118 that in both cases the system keeps its properties constant in time. The radical difference is that in equilibrium there is no change in free energy at all (dF = 0), while in the continuous state this change is continuously going on, but at a constant rate (dF = const).

For clarity, we may cite the following elementary example. A simple bucket of water may serve as the model of a closed static system which maintains its water level constant because of the lack of any processes at all. On the other hand, a circulating basin into which water is continuously flowing from one pipe while it flows out from another is a continuous open system. The water level in such a basin may remain unchanged, but only with a certain constant ratio between influx and efflux rates. By changing these ratios, we can produce any other level, which for the same reasons will preserve its continuous state.

This very simple example uses a system in which no chemical reactions take place.

For the understanding of life processes, however, chemically open systems are of far greater interest. Substances are also continuously entering from the environment into a system somehow separated from it, but these substances are here subjected to chemical changes, and the resultant reaction products are given back to the external medium. Therefore, the constancy of this system in time is characterized by a continuous state in which not only a certain ratio between influx and efflux rates of substances into the system is maintained but also a certain ratio between the rates of the chemical changes occurring in the system.

When the diffusion and reaction rates are constant, the system assumes a

certain stationary state, a certain level of components comprising the system. With any changes in these parameters, the system "equilibrium" is impaired, but then a new continuous state, is established. The number of these possible continuous states is as large as desired. When a catalyst which accelerates a certain reaction is introduced into such a system, a change in the level of the system component ratios may occur. This is quite impossible in closed systems, where the catalyst can merely change the rate at which equilibrium is achieved, but not its position (Ref. 29).

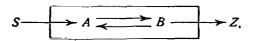
The situation in the living cell is incomparably more complex than in the simplest chemical system which we have cited. Here not one individual chemical /119 reaction is of principal significance, but a whole chain of rigorously interrelated chemical transformations. This chain may be linear, with no branching, or it may branch or even be closed in cycles. A certain repetition in the chemical processes is created in these cycles. However, in their individual links there is always irreversible branching of the processes, and for this reason biological exchange on the whole always proceeds in one direction.

In protoplasm, the numerous chains and reaction cycles are intercombined into a unified, very ramified, regularly constructed network of metabolism, which C. Hinshelwood compares with a well-developed railroad network in which many trains are simultaneously moving at different speeds (Ref. 30).

Viewed from this aspect, a simple solution or uniform mixture of organic substances represents a wide, but completely strange, field of chemical possibilities. We can move over this field in any direction under equally great difficulties, and therefore at an equally slow rate of speed. In contrast to this, there are certain paths followed by biological processes laid down in the protoplasm, a whole network of "rationally constructed tracks", over which are continually taking place chemical transformations of substances and the conversion of energy associated with it at tremendous speed on a "rigorously" maintained time-table. Underlying all this organization of protoplasm in time, there is a relationship between the rates of the interconnected metabolic reactions.

In order that the organization of coacervate droplets may approach that of living bodies, in order that it may to some degree serve even as the simplest model of these bodies, it must pass from the static to the continuous state, and its interaction with its environment must become continuous in character. But this demands that the substances in the solution surrounding the droplet be not only selectively absorbed by it, but that they also undergo certain chemical changes in the droplet.

The relationships hereby created may be shown in the following elementary diagram:



where the rectangle represents a system, (e.g., a coacervate droplet) S and Z are the external medium, A is the substance entering the droplet from the external medium, and B is the reaction product capable of diffusing into the

<u>/120</u>

external medium.

If reaction  $A \to B$  proceeds faster than the inverse transformation, if it takes place in the system at a greater velocity than in the environment, the concentration of substance A in the system is continually dropping, and this impairs the equilibrium between the system and the medium, thus making it possible for more and more new amounts of substance A to enter the system. In contrast, the concentration of B increases in the reaction process, and this causes substance B to enter the external medium. The result of this is that a constant and unidirectional stream of the substance through the system is generated, while its dF is always kept constant by being replenished with energy flowing in with substance A from the environment and being liberated in the system in the A  $\rightarrow$  B reaction process (if, of course, this reaction is exoergic).

The most effective method of increasing the rate of a reaction of this sort in the system is to include the proper catalyst in it, which may be either an organic compound, or an organic salt, or a combination of the two. Moreover, it is quite unnecessary that this catalyst be originally formed in the system itself — it may enter the system in whole or in part from the environment, but it must be gathered there in the same way that dye is stored in the coacervate droplet which absorbs it.

The system which comes about when not one, but two interconnected reactions proceed in the system is somewhat more complex

$$S \longrightarrow A \longrightarrow B \longrightarrow C \longrightarrow Z$$

In this case, depending on the ratio of reaction  $A \to B$  rate to that of reaction  $B \to C$ , substance B may be accumulated in the system or rapidly disappear from it. If, moreover, substance B is a polymer which enters into the composition of the system, the system may enlarge or, on the other hand, diminish its volume and weight.

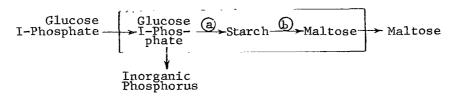
In order to reproduce these effects in simulation experiments, we used coacervate droplets as the systems interacting with the external medium (Ref. 31). In most cases, we formed these droplets by mixing solutions of natural polymers (polysaccharides, proteins, nucleic acids, etc.) isolated from various organisms. Here, of course, we took the fact into consideration that these materials, which are marked by a strictly determinate intramolecular structure, could not have /121 been in the "primary broth" of the Earth's atmosphere, but it was simpler to utilize these objects to establish the phenomena which are inherent in polymers of random structure (this was subsequently corroborated by the above cited special experiments).

Similarly, we used enzyme preparations as catalysts, and not the simpler (but less efficient) accelerators, since this enabled us to conduct our experiments quickly in periods suitable to laboratory conditions (Ref. 32). Later on we propose to replace the enzymes by less advanced organic or inorganic catalysts, but for this initial stage of the investigation the use of natural polymers and enzymes afforded incalculable advantages.

If a preparation of phosphorylase (glucosyltransferase) from potato is added to the coacervate which forms when solutions of gum arabic and histone are mixed at pH 6-6.2, this enzyme is almost entirely concentrated in droplets. When glucoso-I-phosphate is dissolved in the equilibrium liquid, the droplets begin to store starch; this may be very easily detected by an iodine test. The starch increment ina single coacervate droplet can be directly measured by interference microscopy. After only 30 minutes, its weight goes up 50%, while its volume increases by a factor of more than 1.5 (Ref. 33).

Since glucoso-I-phosphate suffers no appreciable adsorption by the abovementioned coacervate droplets, its concentration in the droplets and in the surrounding solution always remains approximately the same. Hence, for such a large quantity of starch to form in the droplet, constantly new amounts of glucoso-I-phosphate must flow into the droplet from the external medium as they are consumed in synthesizing the polymer. When  $\beta$ -amilase is incorporated along with phophorylase in the droplet, the starch forming therein decomposes into maltose which is given off into the external medium where it may easily be detected and measured.

Therefore, the whole process of synthesis and breakdown which we have described may be represented by the following flow-diagram of substances through the coacervate droplet (depicted here as a rectangle).



Depending on the ratio of reaction rates a and b, the quantity of polymer /122 (starch) forming in the droplet from a substance from the external medium may rise or fall, and the droplet may grow or decay. This system may to a certain degree serve as the simplest model of the flow of substances through a living cell.

In similar fashion, we produced both enzymatic decomposition (Ref. 34) and enzymatic synthesis of polynucleotides (Ref. 35), which were one of the components of our coacervate droplets. The decomposition process was effectuated by ribonuclease incorporated into droplets consisting of RNA, serum albumin, and gum arabic. Here the RNA broke down in the droplets, and its products (mononucleotides) were given off into the environment. This can be established by chemical analysis, and likewise may be directly seen in photographs made in the gas chamber of the electron microscope at the beginning and end of the enzyme's action (Figure 19).

The inverse process -- enzymatic synthesis of polynucleotides in coacervate droplets due to monomucleotides being dissolved in the surrounding medium -was produced in our experiments by means of the bacterial polynucleotidephosphorylase incorporated into the histone + RNA droplets. Adenosine diphosphate /123 (ADP) served as the substrate. The droplets stored polyadenine, which in the absence of RNA coacervates with histone to form droplets in which the polymer

is synthesized incomparably more rapidly and intensively than in a homogeneous solution of substrate and enzyme (Ref. 36).

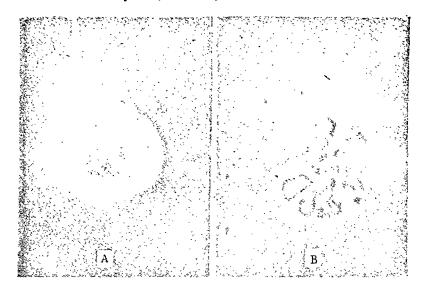


Figure 19. Coacervate Droplet of Serum Albumin + Gum + RNA and the Enzyme Ribonuclease Under the Electron Microscope. (A) - Before beginning of decomposition; (B) After 15 min. of decomposition.

We therefore now have at our disposal dynamically stable coacervate droplets interacting with the external medium like open systems — droplets which are capable not only of maintaining themselves in the steady state, but also of increasing in volume, growing by the accelerated polymerization within them of the substances of the external medium. Droplets of this sort may act as models of the complex multimolecular systems which must have separated out of the aqueous solution of the "primary broth" and been formed from the polypeptides, polynucleotides, and other polymers that came into being in that broth, which were marked by no definite sequence of monomer radicals in their chain.

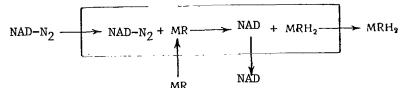
Such models may, to be sure, grow only when the external medium contains phosphorus compounds rich in energy, but, as indicated above (experiments of Ponnamperuma et al.) these compounds must have been abiogenically synthesized in the "primary broth", particularly by the energy of short-wave ultraviolet light. Consequently, their presence in the preactualistic reducing hydrosphere of the Earth was by no means precluded, but there was scarcely enough of them to stipulate the continuous existence of coacerate droplets for a protracted period. After the lapse of some initial period, only those droplets were able to maintain themselves as continuous systems which had the inherent capacity of forming macroergic compounds by processes leading to the liberation of free energy.

Under the reducing conditions of the "primary broth", the most probable of these processes were the oxidizing-reducing reactions associated with hydrogen

or electron transfer.

It is apparently precisely reactions of this sort which were the earliest elements in the metabolism being formed. This is indicated by their striking universality and their obligatory participation in all life processes known to us, in all living beings without exception. It is not without reason that A. Klyuver, on the basis of very extensive comparative biochemical material, (Ref. 37) rightly considered the continuous and directed motion of electrons as the most essential sign of the living state.

Just like polymerization processes, oxidizing-reducing reactions may easily be reproduced in coacervate droplets in simulation experiments. In particular, we produced a system which may be represented by the following diagram (Ref. 38):



The reduced nicotine-amide-adenine- $\underline{\text{dinucleotide}}^*$  (NAD-N<sub>2</sub>) entered the droplet from the external medium and gave up its hydrogen to the dye (MR) adsorbed by the droplet. This MR was reduced and was given off into the external medium.

The process goes on with the liberation of free energy. We accelerated it by including in the droplet oxidoreductase (NAD-N $_2$ -dehydrogenase) isolated by N. Gel'man from the surface membrane of bacteria (Ref. 39). This process may, however, also be realized spontaneously. In the droplets, it occurs considerably faster than in the surrounding medium because of the spatial convergence of the reacting substances (shortening of the electron mean free path).

The energy liberated in electron (hydrogen) transfer is dispersed chiefly as heat. It may be directly used to synthesize macroergic compounds or to form polymers. However, when oxidizing-reducing reactions are combined with phosphorylation (which here can also proceed under anaerobic conditions), the energy of the pyrophosphate and other macroergic bonds is stored. This energy is easily used for polymer synthesis (Ref. 40). Our preliminary experiments in simulating combined anaerobic phosphorylation in coacervate droplets gave positive results.

The flow of substances through the droplet is accomplished in the simple oxidizing-reducing model entirely due to the energy of the reacting substances themselves, which is liberated in the process of electron (hydrogen) transfer. Exogenous energy, e.g., the energy of light entering the droplet, may, however, also be used for this. The source of this energy in the initial periods of the development of life could have been the shortwave ultraviolet light which penetrated deeply into the preactualistic atmosphere. After that, the longwave

/125

<u>/124</u>

<sup>\*</sup> In the old terminology DPN or  ${}^{\rm C}_0{}^{\rm I}$ .

light (with less quantum energy) also began to play a role if it was absorbed by specific substances (pigments) of the droplet. K. Serebrovskaya and V. Yevstigneyev (Ref. 41) reproduced this phenomenon in a simulation experiment by incorporating chlorophyll into the coacervate droplets (Figure 20).

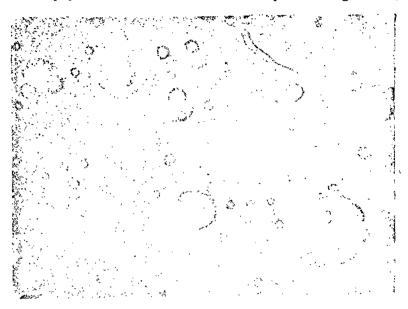
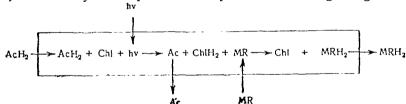


Figure 20. Coacervate Droplets Containing Chlorophyll.

If such droplets are put into a solution of ascorbic acid and methylene red and are illuminated with visible light, an oxidizing-reducing photoprocess occurs in them, which may be represented by the following diagram:



On entering the droplets, the ascorbic acid gives up its hydrogen to the chlorophyll, a process which occurs only with the participation of a light quantum. Then the chlorophyll transfers the hydrogen to the dye coming from the external solution, and is itself regenerated to its original state. The reaction products, Ac and MRH $_2$ , enter the external medium.

<u>/126</u>

In this experiment, the oxidizing-reducing reaction takes place in the droplets tens of times faster than in the outer solution surrounding them.

Photochemical reactions of a similar type could also have taken place in the coacervate droplets of the "primary broth", but in the preactualistic era they were produced by means of the energy of ultraviolet light and did not require chlorophyll (or porphyrine derivatives, in general). In particular, ATP could also have been formed directly in the coacervate droplets by the sort of reactions carried out by Ponnamperuma. The above-mentioned chlorophyll-containing model, however, indicates that at the very beginning of the actualistic era longer wave radiation could be converted to use in photochemical reactions. We are now faced with the problem of combining under laboratory conditions three types of primitive metabolic reactions (oxidoreduction, combined phosphorylation, and polymerization) in a unified coacervate model. It is only a question of time until this model is constructed. It is clear even now that complex systems like it could not only have had a protracted existence, but also could have grown in a solution of the substances whose presence, or even abundance, we have a right to expect in the Earth's "primary broth".

At the same time, the modeling which we have done demonstrates that the regular formation of systems of this sort in the "primary broth" could have occurred naturally. This only required that conditions be created in previously-produced static coacervate droplets for development of reactions which were constantly faster than in the external medium — first polymerization reactions, and then oxidoreduction and the phosphorylation reaction combined with it. But such conditions could easily have arisen, at least in those droplets whose composition enabled them to absorb from the external medium the simplest organic or inorganic catalysts (in the same way as in the simulation experiments with dyes). In this way, the droplets continually maintained in themselves a concentration of the appropriate catalysts which was higher than in the surrounding medium even when the droplets' mass increased with their growth due to polymerization of the monomers of the surrounding solution.

For purposes of convenience, in the following we will give the name of "protobion" to systems of this sort which actively interact with the external medium, possess dynamic stability, and are capable of maintaining themselves and growing under the conditions of the "primary broth".

/127

Protobions already possessed a significantly more complex and advanced organization than did static coacervate droplets, but they were nonetheless many orders simpler than the most primitive living beings.

Only in the course of further evolution were these protobions, which were produced naturally, able to transform themselves into primitive organisms, thus originating life on the Earth. We now still do not know how to reproduce this evolution artificially in simulation experiments, but we can nevertheless with a great degree of probability imagine its subsequent course of development from the extensive data which we derive in a comparative study of different forms of metabolism organization in the most primitive modern organisms (Ref. 42).

## REFERENCES

- 1. Oparin, A. Comp. Biochem. Physiol., V. 4, 377, 1962.
- 2. Goldacre, R. Surface Phenomena in Chemistry and Biology, p. 276, Pergamon Press, 1958.
- 3. Wilson, A. Nature, 183, 318, 1959; 184, 99, 1959.

- 4. Fox, S., Fukushima, T. Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry). Izdatel'stvo "Nauka", p. 93, 1964.
- 5. Young, R., Munoz, E. Cited by Fox, Ibid.
- 6. Fox, S., Harada, K., Kendrick, J. In Preprints Intern. Oceanograf. Congress Amer. Assoc. Adv. Sci., p. 80, 1959.
- 7. Young, R. In the Collection: Origin of Prebiol. Systems. Acad. Press, 1965.
- 8. Oparin, A. Ocherk dialektiki zhivoy prirody (In the Collection: Synopsis of the Dialectics of Living Nature). Izdatel'stvo 'Mys1', 1965.
- 9. Bungenberg de Yong, H. Protoplasma, 15, 110, 1932.
- 10. Bungenberg de Yong, H. La coacervation (Coacervation). Hérmann. Paris, 1936.
- 11. Bungenberg de Yong, H. Proc. Ak. Wetensch. Nederl., 50, 707, 1947.
- 12. Bungenberg do Yong, H. Koll. Zeitsch., 80, 221, 1937.
- 13. Booij, H., Bungenberg de Yong, H. Biocolloida and Their Internations Protoplasmalogia, V. 1, 1962, 1956; Koets, P. J. Phys. Chem., 40, 1191, 1936; Dervichian, D. J. Sci. and its Applic., 2, 210, 1949.
- 14. Serebrovskaya, K. Dissertatsiya (Dissertation). Author's abstract. Izdatel'stvo "Nauka", 1964.
- 15. Perret. C. J. Gen. Microbiol., 22, 589, 1960.
- Oparin, A., Serebrovskaya, K., Vasil'yeva, N., Balayevskaya, T. Doklady Akademii Nauk SSSR, 154, 471, 1964.
- 17. Oparin. A. Origin of Prebiological Systems. Acad. Press, 1965.
- 18. Yevreinova, T. Dissertatsiya (Dissertation). Author's abstract. Moscow State University, 1962; Yevreinova, T., Kuznetsova, A. Doklady Akademii Nauk SSSR, 124, 688, 1959; Yevreinova, T. Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems of Evolutional and Technical Biochemistry). Izdatel'stvo "Nauka", 1964.
- 19. Yevreinova, T., Kuznetsova, A. Biofizika, 6, 288, 1961; Ibid., 8, 395, 1963.
- 20. Oparin, A., Stoyanova, I., Serebrovskaya, K., Nekrasova, T. Doklady Akademii Nauk SSSR, 150, 684, 1963.
  /128
- 21. Yevreinova, T. Doklady Akademii Nauk SSSR, 141, 1224, 1964.
- 22. Bungenberg de Yong, H. Mallee. Proc. Nederl. Ak. Wetens. 56, 203, 1953; Bungenberg de Yong, H., van Someren, C., Klein, .F. Proc. Nederl. Ak. Wetensch., 578, 1, 1954.
- 23. Serebrovskaya, K., Vasil'yeva, N., Mkrtumova, N. Doklady Akademii Nauk SSSR, 29, 910, 1964.
- 24. Yevreinova, T., Pogosova, A., Tsukanova, T., Larionova, T. Nauchnyye Doklady Vysshey Shkoly, No. 1, p. 159, 1962.
- 25. Oparin, A. Zhizn', yeye priroda, proiskhozhdeniye i razvitiye (Life, Its Nature, Origin, and Development). Izdatel'stvo Akademii Nauk SSSR, 1960.
- 26. Heraclitus of Ephesus. Fragments. Translated into Russian by V. Nilender. Izdatel'stvo Musaget, Moscow, 1910.
- 27. Schoenheimer, R. The Dynamic State of Body Constituents. Harvard Univ. Press, Camb. Mass., 1942.
- 28. Prigogine, I. An Introduction on the Thermodynamics of Irreversible Processes, Springfield, 1955.
- 29. Pasynskiy, A., Dechev, G. Izvestiya Akademii Nauk SSSR, Seriya Biologicheskaya. No. 4, 497, 1961; Pasynskiy, A. Uspekhi Sovremennoy Biologii, 1957; Pasynskiy, A., Slobodskaya, V. Doklady Akademii Nauk SSSR, 153, 473, 1963.

- 30. Hinshelwood, C. The Chemical Kinetics of the Bacterial Cell, Clarendon Press, Oxford, 1947.
- 31. Oparin, A. Nova Acta Leopoldina, N. F., Vol. 26, n. 165, p. 87, Leipzig, 1963.
- 32. Oparin, A. Proced. of the International Symposium on Enzyme Chemistry. Tokyo, 1958; Libl, V., Khalupka, N., Molek, I. Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry). Nauka, Moscow, 1964.
- 33. Oparin, A., Yevreinova, T., Larionova, T., Davydova, I. Doklady Akademii Nauk SSSR, 143, 80, 1962.
- 34. Oparin, A., Serebrovskaya, K. Doklady Akademii Nauk SSSR, 122, 661, 1958.
- 35. Oparin, A., Serebrovskaya, K., Auerman, T. Biokhimiya 26, 499, 1961;
  Oparin, A., Serebrovskaya, K., Pantskhava, S., Vasil'yeva, N. Biokhimiya, 28, 671, 1963.
- 36. Serebrovskaya, K. Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry). p. 127, 1964.
- 37. Klyuver, A., van Niel, a.C. The Microbe's Contribution to Biology, Cambridge, Harvard Univer. Press, 1956.
- 38. Oparin, A., Serebrovskaya, K., Pantskhava, S. Doklady Akademii Nauk SSSR, 151, 235, 1963.
- 39. Gel'man, N., Zhukova, I., Oparin, A. Biokhimiya, 28, 122, 1963.
- 40. Kotel'nikova, A. Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry). P. 80, 1964.
- 41. Serebrovskaya, K., Yevstigneyev, V., Gavrilova, V., Oparin, A. Biofizika, 7, 34, 1962.
- 42. Oparin, A., ed. Evolyutsionnaya biokhimiya. Trudy V Mezhdunarodnogo biokhimicheskogo kongressa (Evolutionary Biochemistry. Transactions of the Fifth International Biochemical Congress). Vol. 3, Izdatel'stvo Akademii Nauk SSSR, 1963.

## V. "PROTOBION" EVOLUTION AND THE RISE OF PRIMITIVE ORGANISMS

/129

In our step-by-step study of the evolution of carbon compounds, we have already considered great heights of organization and ascended a number of steps in this organization. In so doing, we have seen that every preceding step in the development served as the basis for the formation of the next. Thus, the appearance of hydrocarbons on the terrestrial surface determined the formation of the "primary broth", in which, along with relatively simple organic substances, there were also polymers similar in type to protein-like and nucleinlike compounds. The formation of this type of high-molecular polymers, although still not possessing the patterned chain-arrangement of monomers, led to the isolation of individual complex formations like coacervate droplets from the common solution of the "primary broth". Even while these formations were originally static in nature, they must subsequently have assumed a dynamic nature. The coacervate droplet or other similar individual system, which had originated in one way or another in the hydrosphere of the Earth and was separated from the external medium, was immersed not simply in water, but in a solution of various salts and organic compounds. These substances penetrated into the droplet,

interacting chemically with each other and with the substance of the droplet itself, thus transforming it into an open system whose very existence depended /130 on the compatibility of the reactions occurring in it. In the absence of such compatibility, but with constant interaction with the external medium, the system would very quickly have had to break down and disappear as an individual formation. If, however, the interaction between medium and system somehow ceased, then such a static system was for this very reason excluded from the general process of evolution.

While thus always staying on the ground of physical and chemical laws, we have arrived at the genesis of "protobions", about whose organization we can to a certain degree form an idea from the models which we have produced.

Even the most primitive organisms, however, profoundly differ from all the above-mentioned systems, including the protobions having exceptionally high "appropriateness" of internal organization determined by the directed nature of their metabolism. The innumerable chemical reactions occurring in living beings are not only strictly correlated into a unified metabolic network, not only harmonically combined into a single order of continual self-renewal, but this whole order is inalterably directed toward a unified goal — the uninterrupted self-preservation and self-reproduction of the whole living system in its entirety, in regular agreement with the conditions of the surrounding external medium (Ref. 1).

We here use the term "appropriateness" (for lack of a better word), to designate the correlation between the organization of the whole system and its self-preservation and self-reproduction. At the same time, this also designates the structural adaptation of its separate parts for the most perfect and correlated fulfillment of those vital functions which these parts perform in the system as a whole.

The great adaptation of the individual organs to executing the functions to be performed by them and the general "appropriateness" of the whole organization comes to the fore with especial clearness even with a superficial acquaintance of the higher living beings. Man had already noted it long ago, and it was expressed in the entelectry of Aristotle. Its essence was mystical and supermaterial until Darwin explained the genesis of this "appropriateness" rationally and materialistically on the basis of natural selection.

But "appropriateness" of organization is inherent not just in higher creatures, but permeates the whole living world from top to bottom, down to the most elementary forms of life. As we saw above, the agreement between structure and function is inherent even in proteins and nucleic acids and manifests itself on the molecular level, but only if these molecules are biogenic in nature, are a /131 creation of life. In inorganic nature, outside of the dependence on life, this "appropriateness" is lacking. We would, therefore, have tried in vain to seek its explanation in the laws of the inorganic world. The genesis of the appropriate intracellular organization characteristic of living beings — biological metabolism and the dynamic structure of the protoplasm associated therewith — can be explained only by the same principles as the origin of the "appropriateness" of the morphological structure of higher organisms, i.e., by the interaction of organism and environment and by the Darwinian principle of natural

selection. This new biological law arose while life was being formed, and subsequently occupied the leading position in the development of all living matter.

The organization of protobions postulated by us in the preceding chapter may serve as the starting point for this sort of evolution on the road to the The principal element in this organization was that the protobions were not only dynamically stable systems, were not only able to maintain themselves for an indeterminate length of time in the "primary broth", obtaining substance and energy from the external medium encompassing them, but also by a certain combination of the reactions occurring in them they possessed the ability to increase in volume and weight, to grow like the coacervate models which we constructed. In this growth, the protobions to a certain degree kept unchanged the organizational forms characteristic of them. In particular, in the synthesis of ever newer polymer molecules, the compositional constancy of the growing protobions was in a certain measure aided by the reproduction (based on complementarity, which was already possible under these conditions, but was still very imperfect) of the polynucleotides contained in the protobion. However, the main factor was that the protobions kept constant the relationships between rates and compatibility of the reactions occuring in them (Ref. 2) was distinguished by the fact that, even when growing, the protobions always maintained within themselves the original high concentration of simplest inorganic or organic catalysts, selectively absorbing them from the external medium (like dye absorption in our simulation experiments).

It is improbable that, under the conditions of the primitive terrestrial hydrosphere, the protobions could have always grown as a single mass. Under the effect of external mechanical forces (for example, impact of waves or surf) they must have been broken up as the droplets of an emulsion are broken up when it is shaken. Moreover, the larger the size reached by an individual protobion in its growth process, the more substantial were its chances of being broken up into smaller daughter formations. These latter must to a certain degree have /132 kept the same organization of interaction with the external medium which was inherent in the original protobion, since they were only simple bits and portions of a formation whose entire mass was relatively uniform.

This phenomenon in its constancy and precision can, of course, in no measure be compared with the self-reproduction of even the most primitive organisms presently existing. In the growth and division of the probions there could very easily occur all sorts of deviations and shifts, particularly during any change in the conditions of their environment. All this taken together must, however, inevitably have led to the rise of a unique "prebiological natural selection" which determined the further evolution of the protobions on the road toward formation of primitive living beings.

At present, a number of opinions have been expressed in the scientific literature on the competency of the use of the term "natural selection" only in respect to living beings. It is an opinion widely held among biologists (Ref. 3), that natural selection, as a specifically biological law, cannot be extended to objects which are not yet alive, and particularly not to our protobions.

It is, however, erroneous to think that living bodies first originated and then biological laws or vice versa, that in the beginning biological laws were

formulated and then living bodies arose. In this aspect, the formulation of the problem is reminiscent of the old scholastic argument about what came first, the chicken or the egg.

Dialectics obliges us to consider the formation of living bodies and the formulation of biological laws as proceeding in indissoluble unity. It is therefore quite permissible to assume that protobions — those initial systems for the formation of life — evolved by submitting to the action not only of intrinsically physical and chemical laws, but also of incipient biological laws including also prebiological natural selection. Here we may cite an analogy with the formation of man, i.e., with the rise of a social form of the motion of matter which is even higher than life. As is known, this form took shape under the influence not so much of biological as of social factors, chiefly the labor of our ancestors, coming into being at a very early state of homogenesis, and improving more and more. Therefore, just as the rise of man is not the result of the operation of biological laws alone, so the rise of living bodies cannot be reduced to the action of only a few laws of inorganic nature (Ref. 4).

<u>/133</u>

To illustrate this, we would like to give the following specific example, which is to a certain degree accessible to experimental verification. Let us suppose that two types of systems (like our models) are present in the same solution. One of these systems possesses a correlated combination of reactions leading to synthesis and growth of the entire system as a whole under the given conditions of the external medium. In the other systems, however, this correlation is impaired, and the processes going on there lead to a relative delay in synthesis or even to the predominance of decomposition. It is understandable that this second type of system will gradually fall behind in its growth and finally disappear, yielding its place to the first type more adapted to the given conditions of existence.

We must understand "prebiological natural selection" only in this elementary sense. It is mainly expressed in the fact that any disturbance of the correlation in reactions must cause death, the disappearance of the given, so to say, "unsuccessful" individual system.

If, on the contrary, in a particular protobion under conditions of a constant or changing environment there is an acceleration of the reactions of oxidation, conjugation, and polymerization; a rise in their correlation; or, in general, a change in metabolism favoring faster system synthesis and growth, then this system has naturally acquired an advantage over the others, and begins to be formed in greater and greater numbers. The gradual improvement in the organization of the overwhelming mass of the growing and multiplying protobions must also have occurred on this basis.

This must chiefly have concerned their catalytic apparatus as the main factor in the organization of metabolism based on the relationship between the rates of the individual reactions comprising metabolism. Of course, at the stage of development which we are analyzing, there could have been no question of such complex substances (endowed with specific intramolecular structure) as the enzymes of modern organisms. The catalysts available to the protobions could have been only the simplest organic substances or inorganic compounds

present in significant quantities in the "primary broth". In particular, the salts of iron, copper, and other heavy metals, for example, could appreciably accelerate the reaction of electron (hydrogen) transfer. To be sure, their /13 catalytic action was incomparably weaker than that of such enzymes as peroxidase or phenoloxidase. They are, so to speak, very "poor" in comparison with enzyme catalysts. However, as demonstrated by W. Langenbeck (Ref. 5), their catalytic activity can be substantially raised when they are combined with certain radicals or molecules.

The reaction of electron (hydrogen) transfer, for example, may thus be accelerated by even an ion of inorganic iron, but this acceleration is very slight. It rises somewhat when iron is combined with pyrrole. If, however, iron is incorporated into a tetrapyrrole compound -- into the porphyrin ring -- then the hemin thus produced will have a catalytic action a thousand times greater than the similar action of inorganic iron. As W. Langenbeck demonstrated, even such a simple organic compound as methylamine can speed up the reaction of decarboxylation of ketonic acids in a similar fashion to that of the enzyme carboxylase in the living cell. By itself, however, methylamine acts in this direction so weakly that this action can be detected only at an increased temperature (under autoclave conditions). The incorporation of a carboxyl group into the methylamine molecule (synthesis of glycocoll) raises its catalytic effect by a factor of almost twenty. It is raised several times more by the incorporation of an aromatic or heterocyclic ring, etc. Using this method and consciously incorporating newer and newer atomic groupings into the initial molecule, Langenbeck produced his noted "artificial enzyme models", particularly the sort of compound whose catalytic effect was many thousands of times greater than the similar effect of methylamine.

This same route of step-by-step improvement of the simplest catalysts could also have been used in the process of protobion evolutionary development based on their natural selection. M. Calvin (Ref. 6) has justly indicated this possibility for the evolutionary formation of biological catalysts. However, simply in solution the individual molecules of the catalysts could not be naturally selected, since the capacity of these molecules themselves to catalyze oxidation, to a better or poorer extent, gave them no advantage with respect to length of existence or increase in number as compared with other similar molecules lacking this capacity. Other relationships were created for the catalysts included in the integral system of a protobion. The individual parts of the complex, /135 catalytically-active molecules dissolved in the surrounding medium could in themselves be almost completely devoid of this activity. However, selectively adsorbed by a protobion, they combined into a catalytically-active complex. (in comparison to the external medium) this complex accelerated polymerization or the other above-mentioned reactions, it was precisely this complex which determined the continuous nature of the system, its dynamic stability, and its capacity for growth (as we have seen in the example of simulation experiments).

From this it is clear that the more advanced a given complex was -- i.e., the more its molecular structure corresponded to its catalytic function and the more this function was correlated with the other reactions proceeding in a given protobion -- the greater were the advantages which this protobion derived, the faster it grew and multiplied. Consequently, it also occupied a leading position in the progressive evolution of prebiological systems.

We can imagine the colossal number of atomic groupings, radicals, organic and inorganic compounds, and their complexes which to some degree possessed the capacity of catalyzing reactions necessary to the existence of the protobions, e.g., the reaction of electron (hydrogen) transfer.

In numerous protobions which were first produced, this transfer function must, of course, have been effectuated by very different catalytic mechanisms whose structure varied greatly depending on the composition of the medium fron which the material was taken for building these chemical mechanisms, and on the individual features of each individual protobion.

Because natural selection, however, always rejected the less perfect mechanisms and destroyed all the systems endowed with them, this multifariousness gradually became more restricted. From the boundless sea of chemical possibilities in the "primary broth", only the few most effective combinations of molecular groupings were selected. Moreover, the earlier in the process of protobion development this standardization of a particular catalytic mechanism was effected, the more universal it was to be for the whole subsequent world of living creatures.

One example which is most striking in this respect must be mentioned here -- NAD (nicotinamide-adeninedinucleotide), which as the universal carrier of hydrogen participates in numerous oxidizing-reducing processes in the living cell (Ref. 7). We find it definitely in all modern living beings without excep-/136 tion, both in microbes and higher plants and animals, both in heterotrophic and in autotrophic plants, both in organisms which ferment and oxidize different sugars and in living beings whose carbon food sources are phenols and other approximate hydrocarbon derivatives.

This indicates that the NAD was chosen by living nature from a multitude of similar compounds long ago at a comparatively early stage in the evolution of organic matter, at the very springs of life. This was, of course, favored by the preeminent possibilities of abiogenic synthesis of adenine derivatives under the conditions of the "primary broth", as we pointed out above. Therefore, the adenine derivatives must have entered the growing protobions from the external medium at the very beginning of protobion genesis. Subsequently, they acquired more and more significance as hydrogen carriers, as they became more complex and adapted to this process.

On the basis of comparative biochemical study of flavin derivatives, similar statements may also be made about these very universal catalysts of oxidizing-reducing processes in contemporary organisms (Ref. 8), and also about coenzyme A (CoA) and several other similar compounds.

The data presented enable us to hypothesize that at a certain stage in protobion evolution the role of the accelerators of the processes occurring in them began to be played by coenzymes, which therefore replaced simpler, but less perfect organic and inorganic catalysts.

Coferments at the present day also play an outstanding role in the metabolism of all modern organisms. They are not very numerous, but any of them is an extremely widespread universal accelerator of biological processes; this implies that they have taken very diverse forms in the formation and development of life (Ref. 9).

It is quite unnecessary that already in the first stages of evolution coferments should have been completely synthesized in the protobions themselves. The constancy of catalyst concentration necessary for the dynamic stability of growing protobions could also be maintained simply by the entry of these relatively complex compounds or their components from the outside medium. Here it must be recalled that many present-day, even highly organized living beings, despite the absolute need of their metabolism for certain coenzymes, are incapable of synthesizing some of them and are compelled to obtain them from their environment in the form of vitamins (Ref. 10).

The formation of processes leading to coenzyme synthesis from simpler and simpler compounds was, however, a significant step forward on the road of progressive protobion evolution. It created the condition making it possible for protobions to live in a medium which was becoming less and less complex in composition, but at the same time it required the correlated interaction of more and more reactions needed for the synthesis.

In his time, N. Horowitz (Ref. 11) on the basis of his research on the fungus Neurospora gave an interesting diagram for this sort of evolutionary complexity of the synthesizing capacity. It may to a certain degree be applied also to the case which we are analyzing of coenzyme synthesis in evolving protobions. The gist of the system is as follows. Let us assume that some simplest organism or at least some open system needs a more or less complex organic compound A to effect its metabolism. If this component is present in finished form in the environment, the system may take it up directly, even without possessing any special chemical adaptations for synthesizing this substance. But if there is an undersupply of substance A in the environment, or in general if it entirely disappears from there, only those systems can continue to exist in which in some way new chemical mechanisms were generated enabling them to synthesize compound A from the simpler substances B, C, or D present in the surrounding solution in sufficient quantity. Subsequently, the same must also be repeated with substance B after it is exhausted in the environment, and so on.

The initial forms of the evolving systems must therefore have been entirely heterotrophic, i.e., completely dependent on the complex composition of the surrounding medium. Subsequent evolution was aimed at developing in the systems more and more complex and multi-stage processes reducing the dependence of the systems on their environment.

To a certain degree, this path of evolution may be demonstrated even by the example of our coacervate models. The droplets possessing only the ability to polymerize could maintain themselves and grow only in a medium containing macroergic phosphorus compounds. The incorporation of oxidizing-reducing reactions and combined mechanisms permitted the droplets themselves to synthesize the macroergic compounds and made it possible for the droplets to grow in a less complex and specialized medium. Similarly, the existence of the protobions which utilized only the ready-made catalysts found in the medium surrounding them to /138 accelerate and correlate the three reactions mentioned was very restricted by this condition. The catalysts themselves could in this case be represented only

by comparatively primitive, slightly specialized substances. A substantial forward step was therefore the synthesis of more efficient catalysts (coenzymes) from less complex environmental components in the protobion itself. However, this required the additional development of a new synthesis reaction in the protobion to be connected to the three previous ones. Thus, the system of metabolic reactions inside the protobions had to become more and more advanced, and hence complicated, as the process of protobion growth and natural selection went on.

Even purely theoretical considerations expressed by a number of modern authors (Ref. 12) force us to assume that the progressive evolution of such open systems as our protobions, in particular, did not travel merely the path of improved correlation of a small number of above reactions, but also was aimed at increasing the number of these reactions, of lengthening the chains formed by them, of ramifying these chains, and of closing them into constant, repetitive cycles. This is in fact confirmed by the presence in all present-day organisms of a very complex metabolic network consisting of a very large number of reactions. In the different representatives of the living world, this network may, as we will see below, take very diverse forms, but as its individual links it must contain the three reaction types of which we have spoken above. These reactions were already inherent in the protobions and comprised the basis of their rudimentary metabolism, but in the process of evolution they have been repeatedly added to and complicated by incorporation of constantly new individual reactions and their combinations.

The longer and more diverse the reaction chains became, however, and the greater the number of them which entered into the metabolic network, the more rigorous had to be the correlation between the rates of the individual reactions, and the more advanced the catalytic mechanisms which were needed to achieve this. Therefore, the few and relatively mildly specialized coenzyme catalysts which had previously existed proved to be inadequate for solving this complex problem. The next very important step in progressive protobion evolution was the creation of a whole arsenal of powerful new enzyme catalysts — i.e., proteins whose intramolecular structure was extraordinarily well adapted to the catalytic functions they were to perform.

Dickson and Webb (Ref. 13) conclude their fundamental book by justly remarking that the problem of the primitive origin of enzymes is one of the hardest questions to solve. They believe it entirely possible that amino acids or their activated derivatives were abiogenically polymerized in the aqueous primary solution of organic terrestrial substances.

Numerous high-molecular polypeptides and various protein-like substances, therefore, could and must have been formed in this solution. However, it is very unlikely that enzymes had their primary origin in this fashion, in the opinion of Dickson and Webb.

Enzymes possess exceptional activity and specificity of their catalytic effect precisely because their intramolecular structure is very perfectly adapted to accomplishing this biological function of theirs, and this adaptation could not, of course, have had a random origin simply in a solution of organic substances.

106

<u>/139</u>

It is true that we have already become familiar, in the example of coenzyme formation, with the possibility that catalytic equipment may adapt in a certain measure to the function which it performed in primitive metabolism. However, first, this formation, as we saw, could not take place simply in the solution of the "primary broth", but in dynamically stable, growing and multiplying protobions on the basis of natural selection of these individual systems. Second, we must form a clear concept of the fundamental difference existing between coenzymes and modern protein enzymes.

Many enzymes (proteides) contain a particular prosthetic coenzyme grouping in the composition of their catalytically active center. In addition to this, in the active centers of both the proteides and the other enzymes (proteins) the side chains of amino-acid radicals containing hydroxyl, amine, carboxyl sulfhydryl, imidozole, indole, and other groupings are also combined, whose chemical properties are well known. In some cases these groupings, like the coenzymes, may also appear as catalysts, but they are very commonplace in respect to their catalytic activity and cannot be at all compared with enzymes themselves, whose capacity to accelerate this or that particular reaction is truly enormous (Ref. 14). The enzyme hexokinase, for example, thus accelerates the interaction of ATP with glucose by a factor of more than  $10^{11}$ . Alcohol dehydrogenase accelerates the oxidation of alcohol more than a billion ( $10^9$ ) times, and so on. The very high specificity of enzymatic action is also absolutely astonishing and  $\frac{140}{140}$  caused Emil Fischer (1852-1919) in his time to utter the aphorism that any enzyme fits its substrate like a key into a lock.

The fact that each specific enzyme catalyzes only a strictly determinate reaction from a multitude of others, potentially possible for a given reaction substrate, has enormous importance for the organization of metabolism, not only from the aspect of total acceleration of the whole vital process, but also from that of the determinate sequence of metabolic reactions and the general direction of metabolism.

What we have said may be illustrated by the following elementary diagram. Let us assume that a certain organic substance A can be converted into substances B, C, D, etc. In the diagram the rates of these conversions are expressed by the radius vectors, whose length accordingly describes the rate of a certain reaction.

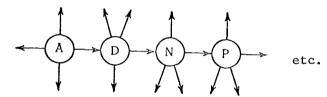


In this diagram we see that the rate of the A  $\rightarrow$  B reaction is seven times greater than that of the A  $\rightarrow$  D transformation, while the latter is twice as slow as the A  $\rightarrow$  C reaction. It is understandable that when, after the lapse of a certain time, the whole reserve of substance A has disappeared there will be 70% B, 20% C and 10% D in the mixture obtained. Therefore, the bulk of substance

A is transformed into substance B, i.e., this transformation takes the path of the fastest reaction.

If in the described case we apply any effects which uniformly increase the speeds of all possible reactions (e.g., a rise in temperature), the ratio between the final product yields will not then change at all. However, if we introduce into the original mixture a catalyst which specifically accelerates only the A  $\rightarrow$  D reaction by many millions of times without touching the A  $\rightarrow$  B and A  $\rightarrow$  C reactions, a completely different effect will be obtained. Here substance A will be practically completely converted into D, while B and C will prove to be only barely perceptible or even imperceptible admixtures.

The substance D thus generated, as well as A or any other organic compound, /141 possesses many chemical potentialities, but it will also chiefly enter into its chemical transformations by the fastest route, while the compound N formed from it may analogously become the initial substance for subsequent chemical transformations. Thus there is generated a chain of successive, temporally intercorrelated reactions whose patterned organization is based on the velocity ratio:

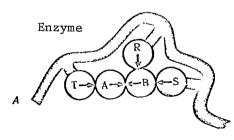


But such a chain is possible only when there is a whole series of catalysts present, each one of which is specific merely to its corresponding link in the chain. The significance of this specificity comes to the fore to an even greater degree in branching of the chains. In this case, not only must the obligatory presence of all catalysts (enzymes) which are specific to each link in the chain be taken into consideration, but also the ratio of their catalytic activity. Any intermediate compound found at the point where the chain branches follows, in practice, not one, but at least two different paths, each of which is determined by its specific enzyme — the relative degree of its catalytic activity. When the number of links in the metabolic chain was small, the metabolic order could be regulated by such relatively backward catalysts as the coenzymes. The metabolic system was able to become more complicated only with the rise of very powerful and rigorously specific catalysts — the enzymes.

At the same time, the coenzymes themselves could be formed only on purely kinetic foundations because of the correlation between the velocities of a relatively small number of reactions. Enzyme synthesis, on the other hand, required far more complex mechanisms determining not only the formation of the molecular groupings comprising the active center, but also the rigorously patterned structure of the whole protein molecule (or at least a considerable part of it) in respect both to the precise sequence of the amino acid radicals in the polypeptide chain, and to the spatial packing of this chain in the protein globule. Although a large number of modern findings indicate that the catalytic activity and specificity of enzyme action is chiefly determined by the active center representing only a very small part of the protein molecule, we nevertheless know that a very important role also belongs to the remaining

/142

structure of the polypeptide chain. It must be regarded as a certain framework whose purpose is reduced to creating the proper spatial arrangement of the groupings determining catalytic activity and specificity.



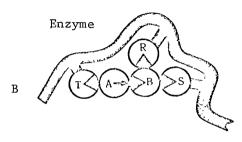


Figure 21. Diagram of Hypothetical Reaction Taking Place on Enzyme Surface with Participation of Two Substrates, A, and B, and of Three Catalytic Enzyme Groups, R, S, and T. The Arrows (A) Indicate Orientation Corresponding to Maximum Reactive Capacity. Darkened Sectors Indicate the Part of the Molecular Surface on which Reaction (B) may Occur. The Active Groups are Kept in their Places by Enzymatic Structural Features: the Substrates -- by Specific Nature of the Adsorptive Processes.

D. Koshland (Ref. 15) believes that the high catalytic qualtities of enzymes are to a considerable degree, and perhaps even entirely, caused by the mutual orientation of substrates and catalyst. As an explanation, he gives a very simple system -- the "triple complex" between two interacting substrates and an enzyme possessing three catalytically active groups distributed in different parts of the polypeptide chain (Figure 21). At the same time. Koshland is of the opinion that the enzyme must not be regarded as a simple "copy" or "mold" of the substrate and that the enzyme configuration under- /143 goes appreciable change during interaction with the substrate. As a model, he gives a comparison with a glove. "A glove", he writes, "is not at all a mold of the hand, and until it is put on the hand it may be folded, twisted, etc. in various ways. Only when it is put on the hand does it completely match it in shape. In the case of the enzyme, similar interrelations obviously occur." This concept of a "flexible" enzyme demands a very perfected degree of order in the structure of the enzymatic protein.

In contrast to this, the arrangement of the amino acid radicals in the originally generated protein-like polymers must have had only a random, disordered nature. These polymers could have served completely as the material for forming coacervate droplets and could have entered into the composition of growing protobions, but they were either completely deprived of catalytic activity or they were very poor catalysts.

Of course, during the continuous polymerization of amino acids entering from the external medium -- a polymerization which was continually proceeding in the dynamically stable droplets or protobions -- individual combinations of amino-acid radicals could also be formed which to a certain degree had inherently useful catalytic activity for the system. This generation of a polypeptide, which was more advanced in this respect, created an advantage for the protobion

engendering it only when, in the further growth of this protobion, the synthesis of polypeptides in it always led to a combination of amino-acid radicals which was constantly favorable catalytically. With the usual "lack of order" in the polymerization of the amino-acids entering the protobion from the external medium, this advantage was quickly lost -- leveled out in the growing protobion.

Thus, it was very important for the further progressive evolution of the protobions that an organization be created which would permit the synthesis of polypeptides already endowed with a certain more or less constant arrangement of amino-acid radicals, and which would secure constancy of intermolecular structure in the newly-synthesized polypeptides. Such an organization could no longer be entirely based on merely kinetic foundations, on the constant sequence of reactions in the chain of metabolism, but required the development of fundamentally new spatial ("matrix") mechanisms. An exceptionally important role in this respect fell to the lot of the polynucleotides.

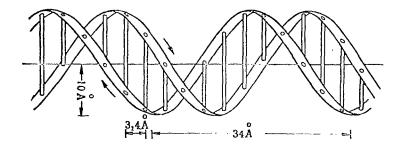


Figure 22. Structural Model of DNA Molecule (According to Watson and Crick).

As was pointed out above, in the earth's original "nutrient broth" only /144 "disordered" synthesis of polynucleotides having mononucleotide radicals randomly arranged in their molecular chain was possible. But as soon as this chain reached a certain size, even the polynucleotides of "disordered" structure having a certain degree of polymerization now entered into reciprocal relations with the polypeptides and other polymers of the "primary broth", and together with them separated out of the common solution in the form of coacervate droplets, as we demonstrated above in simulation experiments.

Polynucleotides, however, differ from other polymers in the following unusual way. More than ten years ago Watson and Crick (Ref. 16), starting from a number of steric and chemical considerations, demonstrated that two polynucleotide chains could combine with each other into a double spiral only in a complementary fashion (Figure 22), i.e., so that a certain purine or pyrimidine base in one chain was joined by hydrogen bonds only to another determinate, but non-identical base of the other chain (e.g., adenine combines with thymine or uridine, but guanine always with cytosine) (Figure 23). This hypothesis was experimentally corroborated first in simple synthetic polynucleotides composed entirely of identical mononucleotide radicals alone. It was, for example, thus shown that polythymidylic acid is complementary to a polynucleotide chain containing no other bases but adenine (polyadenylic acid). Subsequently, by the

example both of natural nucleic acids (DNA) and of artificial polynucleotides constructed of all four bases, clarification was obtained for the role which is played by the complementarity of polynucleotide chains in their syntheses, when the sequence of bases in one such chain determines their sequence in the other /145 also (Ref. 17).

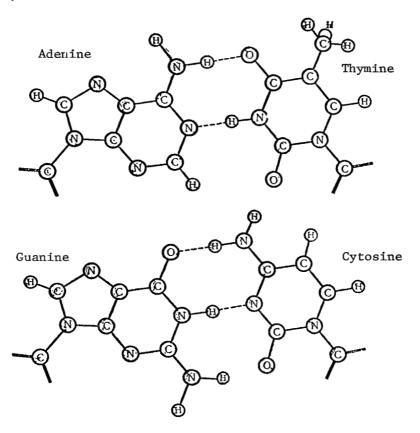


Figure 23. Hydrogen-Bond Formation Between Purine and Pyrimidine Bases.

G. Schram et al. (Ref. 18) found that this phenomenon also occurs in abiogenic non-enzymatic synthesis of polynucleotides. In his experiments, for example, in the polycondensation of uridine monophosphate the synthesis of uridylic acid thus proceeded many times faster in the presence of its complementary polyadenylic acid and, contrariwise, the formation of uridylic acid accelerated synthesis of the polyadenylic chain.

In the simple aqueous solution of the "primary broth", this sort of accelerated formation of any certain single polymer could have caused it only to accumulate constantly in the form of unusual organic deposits. Even if some /146 random changes occurred in these syntheses -- for example, incorporation of other mononucleotides into the originally uniform chain -- these "mutations", so to speak, could play no role in the further evolution of organic matter. The

fact that one or several adenine radicals were replaced by other bases in the polyadenylic chain gave this chain no advantages over the former unaltered chains in their subsequent "multiplication". Therefore, under the conditions of a simple aqueous solution no selection of individual polynucleotide molecules could occur. Quite different relationships were created when these molecules were incorporated into integral systems containing other polymers — in particular, protein-like polypeptides — as occurred in the formation of coacervate droplets in the "primary broth".

In this case, any sequence of mononucleotides in the polynucleotide chain could affect the combination of active amino-acid groups in the polypeptides forming in the system, and this combination exerted its influence on the primitive metabolic organization of the entire given system as a whole. If the changes thus occurring in metabolism were favorable in the sense of maintaining and increasing the integral system, they were retained by natural selection and became fixed in the given growing system because of reproductions of the polynucleotides formed. In the contrary case, they were excluded from subsequent protobion evolution, because the system giving rise to these changes perished. Therefore, it was not the polynucleotide chain itself, as such, which was subjected to selection proper, but the integral system in which this chain had produced a certain metabolic change.

Owing to the advances achieved by biochemistry in recent years (Ref. 19), we know that in present-day organisms the synthesis of proteins, which have a certain sequence of amino-acid radicals in their polypeptide chain, particularly the synthesis of enzymes, is realized by an extraordinarily complex and refined mechanism pre-existing in any cell (Ref. 20), having the simplified system which we present in Figure 24.

This mechanism includes about twenty different specific enzymes activating amino-acid, approximately twenty different specific types of dissolved ribonucleic acid of low molecular weight (S-RNA) (the so-called transfer RNA) and a certain type of matrix determining the sequence of amino-acid threading in the protein chain. Large molecules of informational m-RNA, exercising their function on /147 specific subcellular particles -- ribosomes -- apparently serve as these matrices. The m-RNA molecules themselves are synthesized in the cell nuclei under the control of DNA, which itself performs two functions -- first, it ensures reproduction of itself by copying during cell division, retaining the arrangement of mononucleotides in the chain characteristic of the original molecule in the newly-formed molecules. Second, DNA possesses the capacity to construct complementary chains of m-RNA depending on its own structure, and to determine (by means of the m-RNA) the order of amino-acid arrangement in protein synthesis (Ref. 21). Besides these substances and chemical mechanisms, a certain set of enzymes is probably still required to synthesize the peptide bond, to remove the finished protein molecule from the ribosomal matrix, as well as to reactivate the S-RNA. At the proper stages in the synthesis, moreover, energy must be delivered to the system in the form of adenosine triphosphoric acid (ATP) synthesized in the mitochondria.

Protein synthesis probably proceeds as follows. First, the amino acid, activated by reaction with ATP, forms aminoacyladenylate. Effectuation of this stage requires the presence of an enzyme, and apparently different enzymes are

required for different amino acids. The aminoacyladenylate, which apparently remains fixed to the activating enzyme, is then transferred to the S-RNA. After that, every particle representing a complex of S-RNA plus activated amino acid is bound to a specific location on the matrix m-RNA on the ribosome. The amino acids are thus gathered into the polypeptide chain in a definite order depending on the arrangement of the mononucleotide radicals in the polynucleotide m-RNA chain. Thus, in principle, a certain mononucleotide triplet in the m-RNA chain corresponds to a certain amino acid (or, more precisely, to its complex with S-RNA). For example, guanine, uracil, adenine (GUA) correspond to aspartic acid; cytosine, cytosine, guanine (CCG) correspond to alanine; uracil, uracil, uracil (UUU) correspond to phenylalanine, etc. (Ref. 22).

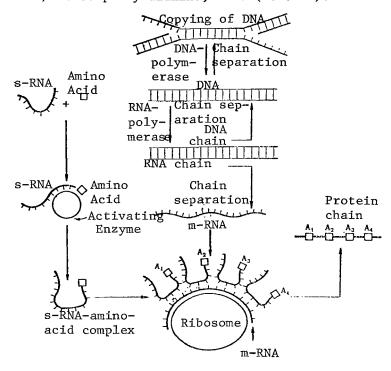


Figure 24. Diagram of Protein Synthesis (According to A. Rich).

It is quite clear that this type of exceptionally complex and refined protein-synthesizing apparatus in advanced organisms could have formed only as the result of a very prolonged evolution of pre-existing systems, whose stability was originally chiefly dynamic in nature and depended on the correlation between the metabolic reactions taking place therein and interaction with the external medium. The development of a three-dimensional "molecular-matrix" /148 apparatus was a supplementary superstructure raising this most ancient form of organization to an unprecedented new height of perfection in the correlation of chemical processes and in the refinement of system self-reproduction, but in principle this superstructure maintained the previous dynamically stable nature of the living beings thus formed.

B. Commoner (Ref. 23) correctly cautions against too great enthusiasm for the matrix concept of self-reproducing RNA, and points out that in relation to biological systems this would inevitably lead to preformation. Even in advanced organisms, we must not entirely reduce the whole specific nature of protein synthesis to only spatial organization of macromolecules, to matrix copying. An important part in this process is also played by the kinetic properties of the reacting systems, not merely the structure of the initial molecules. This is all the more true of systems preceding the appearance of life. Therefore, the genesis of rigorously ordered polynucleotide chains, spatial matrices for protein synthesis, was by no means the initial point of departure in prebiological /149 evolution, but, on the contrary, was its highest finishing stage.



Figure 25. Ribosomes from Bacterial Cell. X 300.000

A. Rich has recently given a very interesting outline of this sort of evolution in his article summarizing this question (Ref. 24). However, Rich imagines this evolution as proceeding in its entirety only on the molecular level, as a process of gradual complication and ordering of the intramolecular structure of polynucleotides and polypeptides on the basis of their natural selection outside of any integral systems.

In contrast to this, it seems to us that, first, the interaction of polypeptides and polynucleotides of the "primary broth" having an ordered structure would necessarily have had to lead to the formation of individual multimolecular systems (coacervates and protobions). Secondly, it was not individual molecular/150 structures which were subjected to natural selection, but precisely these individual dynamic systems, depending on the ability of their primitive metabolism to adapt to the problem of the preservation and growth of the system under given

environmental conditions.

From all that has been set forth, we could (of course, very hypothetically) mark out certain successive stages in the prebiological evolution of the proteinsynthesizing apparatus in the very first stage of this evolution. The nucleotide monomers which were dissolved in the "primary broth" gathered into polynucleotide chains of orderless construction, abiogenically independent of any catalytic action of protein-like substances. Rich, taking advantage of A. Kornberg's experiments on AT-copolymer synthesis with no inoculation, as well as the findings on the separation of polymers of this type from certain organisms (Ref. 25), enunciates the very interesting hypothesis that the structure of the primary nucleotides could have been far more monotonous than in modern nucleic acids. Thus, for example, the primary polynucleotides could have contained only two complementary bases -- adenine and thymine -- which are comparatively easily produced under abiogenic conditions. Similarly, the polypeptides of disordered structure which were abiogenically synthesized simultaneously with, but quite independently of, polynucleotides in the "primary broth" could also have been more monotonous. The reason for this could, in particular, have been the fact that not all the twenty amino-acids of the present-day protein molecule were necessarily formed abiogenically under the effect of ultraviolet light or electrical discharges in the atmosphere.

As the above-mentioned experiments in our laboratory have shown, however, molecules even of this sort of very primitive polymers of monotonous and discordered structure in amino acids and mononucleotides, when they were simultaneously synthesized in a common solution and reached a certain size, by necessity combined into multimolecular swarms and separated from solution in the form of coacervate droplets. The formation of these systems was of great assistance in accelerating polymerization, but within the droplets this polymerization of primitive peptides and nucleotides could take place entirely independently from each other. At first they contributed to polymerization, and then it was entirely determined by the combined energy reactions arising in the droplets and protobions. The rate of these reactions in the system depended on the entry of primitive catalysts and coenzymes into it, while the amino-acid polymers could /151 play only an insignificant and fortuitous part. Likewise, the role of primitive polynucleotide copying was also small.

In the second stage, the significance of the interaction of the diverse polymeric molecules gradually becoming more complicated began to manifest itself. Even in modern organisms we can detect synthesis of polypeptides and specialized proteins having a comparatively very simple chemical structure, outside the ribosomal-matrix apparatus, but with obligatory nucleophosphate participation.

In several microorganisms we have thus, for example, established a polypeptide synthesis proceeding along the pattern of nucleoside-triphosphate + amino acids  $\rightarrow$  nucleoside-diphosphate + peptide + orthophosphate. For each of the four nucleotide-triphosphates (ATP, GTP, CTP, and UTP) there is a certain group of amino acids which it can activate (Ref. 26). Polypeptide structure is thus in a certain measure determined by the nature of the nucleoside-triphosphate participating in the reaction.

If, in a system like our protobion, the nucleotide participating in polymer formation has ribose in its composition, then the 3'- and 5'- hydroxyl groups are utilized in the polymerization process, but the third group in the 2' position remains free and through an ether bond can attach itself to the amino acid corresponding to this nucleotide. "It may be assumed," writes Rich, "that it is right at this stage that the system begins to organize itself in which polymerization of the nucleic acid molecule proves to be bound to the 'assemblage' of a certain sequence of amino acids. Only after the amino acids have been gathered into a linear sequence, due to attachment to adjacent nucleotides, can they be polymerized." It is therefore easy to understand how the monomer sequence in the polynucleotide could to a certain degree determine a certain order of amino-acid radical arrangement in the synthesized polypeptide.

It is, however, right here that the fundamental difficulties also begin for the hypothesis which considers the whole phenomenon on the molecular level. In this case it is necessary that the polypeptide thus synthesized in turn effect polynucleotide synthesis and be the specific catalyst of this process. Only in so doing would it have certain advantages with respect to prebiological selection. In contemporary organisms, this actually takes place, but under the conditions of the simple solution of the "primary broth" this sort of adaptation is extremely improbable and seems to be an exceptional "happy chance". Completely different relationships are established if we scrutinize all the /152phenomena in the integral dynamic system -- in the growing and multiplying protobion. In this case, the combination of amino-acid radicals arising under nucleotide influence was also directly to influence nucleotide polymerization, but this combination -- in the same fashion as the coenzymes entering the given protobion or synthesized in it -- catalyzed various reactions occurring in the protobion. If acceleration of a given reaction in conjunction with other processes in the protobion was favorable to the protobion's existence, the protobion obtained an advantage over other similar systems in rapidity of growth and multiplication.

In the opposite case, if the amino-acid order which arose was devoid of useful catalytic activity for the protobion, or if this activity reduced the dynamic stability of the system, this amino-acid combination disappeared under the action of natural selection together with the system which produced it.

Therefore, it was not the various polynucleotides capable of reproduction — or even the polypeptides generated under polynucleotide influence and endowed with a certain sequence of amino-acid radicals — which were exposed to selection proper, but integral systems, the protobions, with primitive, but more or less refined metabolism corresponding or not corresponding to the given conditions of existence. The role of the polynucleotides in this case was spatially to strengthen the constant synthesis of catalytically suitable amino-acid combinations in the growing and multiplying protobions, to serve as a stabilizing factor during their evolution.

On this basis the simultaneously occurring gradual complication and improvement of both polynucleotides and polypeptides proceeded -- lengthening of their chains, enlarging the diversity of the links incorporated into these chains, and establishing a certain rigorous sequence of arrangement of these links in the polymer chains.

Molecules of the protein-like polymers as well as of the polynucleotides controlling their synthesis, became more and more ordered, more and more adapted to the functions which they performed in the evolving prebiological and biological systems. This laid the groundwork for the development of enzymes, whose adaption to their catalytic functions continually improved in the course of evolution. At the same time, polynucleotides also evolved whose complex functions were subsequently subjected to profound differentiation in the process which represented/153 the third and concluding stage in the refinement of the protein-synthesizing apparatus.

In present-day organisms, we have two types of nucleic acids —— DNA and RNA —— with profoundly different functions despite the great chemical similarity of their molecules. Deoxyribo nucleic acids became functionally specialized in the cycle of molecular duplication. Due to the lack of a hydroxyl group at the second carbon atom in deoxyribose, DNA is incapable of affixing amino acids to itself, and therefore cannot directly participate in protein synthesis. However, since it is comparatively very inert in metabolic terms, it provides relatively high constancy of self-reproduction and transmission of the genetic information contained in its polynucleotide chain to the ribonucleic acids by means of duplication. The function of the ribonucleic acids directly involves protein synthesis, and the establishment of a rigorously determinate arrangement of amino-acid radicals in their molecules.

It must be noted, however, that this functional specialization of RNA is not absolute. In principle, RNA can carry genetic information, as occurs, for example, in the case of RNA-containing viruses.

There is therefore reason to assume that the initial forms of the nucleic acids were RNA-like polymers capable both of storing and transmitting hereditary information and of organizing the amino-acid sequence in protein synthesis. Distribution of these functions between the two nucleic acids — the less metabolically active of which specialized in self-reproduction, and the other in direct participation in protein synthesis — is a very progressive step in the process of evolution, and therefore was reinforced by natural selection (Ref. 27).

It is understandable that modern protein-synthesizing systems and the enzymatic proteins resulting from their action are the end result of complex competition between many different systems beginning at a very early stage in the development of life. It is particularly necessary to understand clearly that, between the original polypeptides of low catalytic action and the very ideally constructed modern enzymes, no fewer — and perhaps considerably more — organizational variants were tested and rejected during protobion evolution than, for example, between the shark's fin and human hand. The overwhelming number of catalytic variants which arose in the process of evolution was destroyed by natural selection. Therefore, from modern organisms we now extract only enzymes which are very refined in structure, although when studying /154 the problem more closely we can even today note a certain evolution of these catalysts (Ref. 28).

This pertains to an even greater extent to the evolutionary development of the combination of individual enzymatic reactions in the total organization of metabolism and to the gradual formation of three-dimensional macrostructures in contemporary living beings existing at different stages of evolutionary development. The basic principles of this organization in space and time were laid down as far back as the process of gradual protobion development, and they are therefore common to all living beings.

Later on, however, the evolutionary development of the most primitive organisms which arose on this base proceeded along different paths, and we may form a concept of this development, and consequently of its sources, on the basis of the enormous factual material which has now been amassed by modern comparative biochemistry.

## REFERENCES

- 1. Oparin, A. Zhizn', yeye priroda, proiskhozhdeniye i razvitiye (Life, Its Nature, Origin, and Development). Izdatel'stvo Akademii Nauk SSSR, 1960.
- 2. Eakin, R. Proceed. of the National Acad. of Sci. USA, 49, 300, 1963.
- 3. Mora, P. Proceed. Conf. "Origin of Prebiological Systems" Wakulla Springs, Florida, 1963, Acad. Press, 1965; Gavaudan, P. Foreward to the French edition of A. Oparin's book Vozniknoveniye zhizni ("The Rise of Life"). 1965.
- 4. Oparin, A. Zhizn' kak forma dvizheniya materii (Life as a Form of Matter Motion). Izdatel'stvo Akademii Nauk SSSR, 1963.
- 5. Langenbeck, W. Die Organischen Katalysatoren und ihre Beziehungen zu den Fermenten (Organic Catalysts and Their Relations to Enzymes), 2nd Edition, Springer, Berlin, 1949; Adv. in Enzym., 14, 163, 1953; Nikolayev, L. Vestnik Akademii Nauk SSSR, 3, 13, 1960.
- 6. Calvin, M. Amer. Sci., 44, 248, 1956; Science, 130, 3383, 1959; Calvin, M. Problemy evolutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry), Izdatel'stvo "Nauk," p. 34, 1964.
- 7. Kaplan, N., Swartz, M., French, M., Ciotti, M. Proc. Nat. Acad. Sci., 12, 481, 1956.
- Mahler, G. Conferences et Rapports de 3-me Congrès Intern. de Biochimie (Conferences and Reports of Third International Congress of Biochemistry), p. 264, Liege, 1956.
- 9. Yurkevich, A., Severin, Ye., Braunshteyn, A. Fermenty (In the Collection: Enzymes). Izdatel'stvo "Nauka," p. 147, 1964.

  O. "Biochemistry and Physiology of Vitamins." In the Collection: Catalytic
- 10. "Biochemistry and Physiology of Vitamins." In the Collection: Catalytic Functions of Vitamins. Izdatel'stvo Inostrannoy Literature, 1953.
- 11. Horowitz, N. Proc. Nat. Ac. Sci. US. 31, 153, 1945; Horowitz, N., Miller, S. Current Theories on the Origin of Life. Springr. Verl., Vienna, 1962.
- 12. Pringle, J. New Biology 16, 54, 1954; Perret, C. J. Gen. Microbiol., 22, 589, 1960.
- 13. Dickson, M., Webb, E. Enzymes. Izdatel'stvo Inostrannoy Literatury, 1961.
- 14. Koshland, D., Cellular, J. Comp. Physiol. Suppl. 1, 47-217, 1956; Advances in Enzymology, 22, 45, 1960.
- 15. Koshland, D. V sb: Gorizonty biokhimii (In the Collection: Horizons of Bio-chemistry). Izdatel'stvo "Mir," p. 202, 1964.
- 16. Watson, I., Crick, F. Nature, 171, 737, 964, 1953.
- 17. Kornberg, A. Science, 131, 1503, 1960; Ochoa, S. Nobelstiftelsen (The Nobel Institute), Stockholm, 1960.

- 18. Schram, G., Grotsch, H., Pollman, W. Angew. Chem., 73, 619, 1961.
- Belozerskiy, A. Nukleinovyye kisloty i ikh biologicheskoye znacheniye (Nucleic Acids and Their Biological Importance). Izdatel'stvo "Znaniye," 1963.
- 20. Webster, G. Ann. Rev. Plant. Physiol., 12, 113, 1961.
- Crick, F. Struktura i funktsii kletki (In the Book: Structure and Functions of the Cell). Izdatel'stvo "Mir," p. 9, 1964; Nierenberg, M. Ibid., 1964.
- 22. Ochoa, S. V sb: Gorizonty biokhimii (In the Collection: Horizons of Biochemistry). Izdatel'stvo 'Mir," 1964.
- 23. Commoner, B. Ibid.
- 24. Rich, A. Ibid.
- 25. Sueoka, N. J. Mol. Biol., 3, 31, 1961.
- 26. Bogdanov, A. Tezisy dokladov na I Vsesoyuznom biokhimicheskom s'yezde (Abstracts of Reports at the First All-Union Biochemical Congress). January 1964. No. 1. Izdatel'stvo Akademii Nauk SSSR, p. 13, 1963.
- 27. Spirin, A. Ibid.
- 28. Kaplan, N. Trudy V. Mezhdunarodnogo biokhimicheskogo kongressa. Simpozium III (Transactions of the Fifth International Biochemical Congress. Symposium 3). Izdatel'stvo Akademii Nauk, p. 101, 1962.

## VI. SUBSEQUENT EVOLUTION OF PRIMARY ORGANISMS

/156

The chemical history of the development of life on Earth could have been terminated by the formation of the primary organisms. Thereafter, matter entered a new biological stage of development, and there began the evolution of living beings from the most primitive organisms to contemporary highly organized plants and animals.

An attentive study of this purely biological evolution, however, can give us very much to help us understand the very origin of life, its initial formation. We are unable to observe this process directly in nature since all its intermediate links — the most primitive imperfect forms of the organization of living matter — have long ago been destroyed, swept from the face of the Earth by natural selection, and have apparently not even left behind reliable fossil traces. Nevertheless, these traces have been preserved in the organization of the protoplasm of creatures contemporary with us.

"Among all natural systems," writes E. Zuckercandle and L. Pauling (Ref. 1), "only living matter is distinguished by the fact that, in spite of the very substantial transformations it has undergone, it retains the greatest amount of information reflecting its history written in its organization."

Therefore, by studying this organization we may derive certain objective /157 data on the very earliest forms of the existence of life on Earth. The study of metabolism in particular, that regular sequence of biochemical processes which underlies the organization of everything alive, provides us with a great deal in this respect (Ref. 2). The primitive forms of metabolism, and the definite patterns followed by the combination of oxidoreduction, conjugation, and polymerization reactions were already inherent in the most primary organisms, but during biological evolution they were continually supplemented with new links in metabolism and new internal chemical mechanisms -- catalysts, coenzymes, polynucleotides, enzymes, supramolecular structures, etc. -- stipulating these links.

This enabled the newly-formed living creatures to utilize more advantageously the ever broader circles of the sources of matter and energy necessary to life, to depend less and less on the composition of the surrounding medium, and less and less to run the risk of annihilation when that composition changed in a particular way.

Modern comparative biochemical research fully demonstrates (Ref. 3) that the new biochemical reactions and their combinations arising during evolution by no means always completely replaced previous metabolic links, but -- merely supplementing them -- they were seemingly additional "superstructures" on older forms of metabolism.

We can therefore rather clearly bring these forms to light by studying metabolism in present-day organisms and attempting to determine the traits of similarity in the vast variety of modern metabolic systems, the organizational traits most common to all living beings without exception (Ref. 4).

As the anatomist, studying and comparing the organic structure of individual animals, reproduces the picture of their evolutional development and permits us to look into their distant past, so also the biochemist, by comparative study of metabolism in different organisms may approach the very well-springs of life and understand the most primitive forms of the organization of life.

In such an approach, the following two cardinal assumptions are clearly apparent: (1) the metabolism of all present-day living creatures is based on the form of organization which is adapted to the constant utilization of finished organic compounds as the initial structural material for biosynthesis of proteins, nucleic acids and the other component parts of protoplasm, and as the direct source of energy for these biosyntheses. The vast majority of biological /158 species now populating our planet can, in general, exist only when they are continuously supplied with finished organic substances from their environment. includes all the higher and lower animals, including also most Protozoa, the enormous majority of bacteria, and all species of fungi. Just this fact alone is extraordinarily indicative, but also the same reaction links and the same chemical mechanisms as in the other -- heterotrophic -- living creatures underly the metabolism of green plants and other autotrophic organisms which have already perfected in themselves the capability of synthesizing organic substances from CO2, water, and mineral salts. Autotrophic mechanisms appear in the organisms endowed with them only in the form of a supplementary superstructure on this Therefore, under certain conditions they can easily be disunderlying base. engaged from metabolism, and nevertheless the organisms will not perish, but will merely change to feeding entirely on exogenic organic substances (Ref. 5).

This may be demonstrated with particular simplicity by the example of the poorly organized photoautotrophs — algae — both under natural conditions and in the laboratory. Experiments of this sort long ago established the fact that when organic substances were introduced into sterile algae cultures the algae directly assimilated these substances. This assimilation may take place parallel to the process of photosynthesis, but in some cases photosynthesis may be completely disconnected, and the algae may be transferred entirely to a saprophytic form of life (Ref. 6).

Many species of blue-green and other algae apparently even under natural conditions use the organic substances of contaminated basins of water to feed themselves directly. This is graphically indicated by the very fact that they develop with particular luxuriance in sewage and in other similar locations rich in organic substances.

We may also find heterotrophic bases of alimentation in the higher plants, although in them the photosynthetic apparatus has already reached the apex of its development. The higher plants, however, possess this apparatus only in their chlorophyll-carrying cells, but all the remaining colorless tissues construct their metabolism around the use of organic substances coming to them from the photosynthesizing organs, as is usual for all other living beings. Leaves, in particular, also change to the same sort of metabolism when they are deprived of light.

This situation solidly corroborates the ideas on the development of the original living beings, as we have presented them in the foregoing chapters. Assimilation of organic substances dissolved in the surrounding aqueous medium and conversion of them into component parts of the entire body is, of course, a perfectly necessary initial form of metabolism in all primitive organisms. It was borrowed by them from the protobions themselves, which were capable of incorporating organic substances of the "primary broth" into themselves. Subsequent evolution was at first reduced to selection of the organizational forms which permitted faster and better assimilation of these substances.

(2) In all contemporary organisms, their biochemical systems which derive the energy necessary for life from organic substances are based on remarkably similar mechanisms of anaerobic decomposition of these substances. We may easily ascertain this by thoroughly studying the biochemical processes of metabolism in all present-day organisms, both higher and lower.

Most of these organisms, to be sure, are now absolute (obligate) aerobes, and only a very limited number of modern primitive biological species can long exist without free oxygen or even do not need this gas at all, leading an exclusively anaerobic mode of life. Such a situation is quite understandable for the modern era. Respiration is an incomparably more efficient energy process than is anaerobic metabolism. Therefore, as soon as free oxygen appeared in the terrestrial atmosphere, organisms in the process of evolutionary advancement had to adapt themselves extensively to the aerobic mode of life. It is very remarkable, however, that the energy-producing metabolism of all advanced aerobes is based on the same reaction chains consuming free 0, as that of primitive anaerobes. The reactions of oxidation with gaseous oxygen which are specific to aerobes merely supplement this anaerobic mechanism which is absolutely universal to everything alive. In contrast to this anaerobic mechanism, the oxidational "superstructures" are far from being universal. In the diverse groups of present-day organisms, they differ substantially among themselves. Thus, for example, the polyphenoloxidases characteristic of the higher plants are lacking in the respiratory mechanisms of animals, where their own terminal oxidizing enzymes are in operation.

We therefore see that combinations of anaerobic reactions lie at the root

/159

of the whole "trunk of the tree of life", while the respiratory mechanisms became articulated with them later when this "trunk" divided into individual "branches", into individual groups of more highly organized living beings. of these groups then solved the problem of utilizing the free oxygen which originated at a certain period in the Earth's existence by their own methods specific to the problem (Ref. 7).

/160

These findings of evolutional-biochemical analysis are perhaps one of the most convincing proofs that life originated under the conditions of the reducing atmosphere and hydrosphere, since -- if we assumed that this event had occurred in the presence of free oxygen -- the actual relationships between anaerobic and aerobic metabolic mechanisms in organisms now living would be completely incomprehensible. In exactly this way, the above-cited data on the heterotrophic bases of alimentation also convince us that organic substances in the external medium surrounding the organisms, substances which were abiogenically generated or brought to Earth, served as the initial source of energy and building materials for the original living beings.

Hence evolutional-biochemical research on organisms now living to a certain degree permits us to form a concept of the organizational principles of the original living beings which long ago disappeared from the face of the Earth and which, of course, possessed far more primitive metabolism than any modern microbes, and in this respect significantly approached our hypothetical protobions. Like these protobions, the primary organisms were heterotrophs and anaerobes, but they constructed their catalytic apparatus on the basis of sequential ordering of the intramolecular structure of polypeptides and polynucleotides capable of reproduction, which were responsible for establishing a catalytically advantageous arrangement of the amino-acid radicals in subsequent protein synthesis and in the process of organism growth and multiplication. The set of enzymes which was continually refining itself on this basis permitted the original organisms possessing them to combine a greater number of links in their metabolism and to create long chains of well-intercorrelated reactions, which made the utilization of substances from the environment considerably more efficient and favored more rapid growth and multiplication.

In modern heterotrophic organisms which have traveled a long road of development, we find an organizational form of constructive metabolism in which the initial substances for synthesis of all the complex ingredients of the protoplasm are very simple, low-molecular compounds, such as ammonia, acetic acid, glycocoll, succinic acid, ketonic acids, etc. (Ref. 8). These substances are generated as fragments of nutrient sources which have come in from the external medium and are being broken down in destructive metabolism. Therefore, in modern metabolism the constructive and destructive aspects of metabolism are interconnected in the most initmate way and constitute only two sides of a unified process.

/161

This sort of metabolic organization, however, requires a very complex, multi-membered system of reactions where the immense number of individual chemical acts are continually correlated with each other in time in an exceptionally precise and rigorous manner. It was toward development and refinement of this sort of multi-membered system that the progressive evolution of the original organisms proceeded.

The combinations of oxidoreductive reactions, conjugation, and polymerization inherent in them in the course of further evolution continually were supplemented and complicated by new reactions and their combinations. In modern organisms, we therefore detect the original simplest reactions only as the component elements of the total metabolic system, only as individual, although very important, links in long reaction chains and cycles.

Various carbohydrates entering the organism from the environment or synthesized by the organism itself serve as the principal source of carbon nutriment and the basis of energy-producing metabolism for the vast majority of contemporary organisms. It is difficult to say whether it was precisely this form of metabolism which lay at the very basis of the yet unbranched trunk of the "tree of life", or whether it was only a very early and major branch of it.

A certain doubt as to the primary nature of the monopoly exercised by carbon nutrition is induced in particular by metabolic research in a number of microorganisms isolated from the soils of petroliferous regions (Ref. 9). These living beings are incapable of assimilating sugar, and the hydrocarbons of petroleum and their closest derivatives, i.e., like paraffins, phenols, toluene, salicylic acid, and so on are their sole source of carbon and energy. There are, unfortunately, no absolutely valid data which would permit us to state confidently whether these organisms are some offshoots of the "central trunk of the tree of life" which have come directly down to us, or whether their unique form of metabolism was secondary in origin. In either case it is very significant that inherent in them also are the basic hydrogen carriers in the reduction-oxidation reactions and the "conjugating" energy-producing mechanisms common to the whole animate world (Ref. 10).

But, however that may have been, we may still assume that the main branch of the "tree of life", which during the further evolution of life was almost monopolistic in its development, was the carbon branch of energy-producing metabolism. It is obvious that even at the very base of this branch a certain very complex combination of reactions took shape — a multilinked chain of chemical conversions inherent in all, even the most primitive, organisms now living which could be discovered, so to speak, at all depths of biological evolution (even the most profound), to which only our modern comparative—bio—chemical sounding line can descend. This is the chain of reactions transforming glucose into pyruvate which is depicted in Figure 26. It consists of ten main reactions whose velocities are so intercorrelated that they replace each other in a strictly determinate sequence.

The chief position in this chain is occupied by the hydrogen transfer and "accumulation" of energy which is accomplished with the participation of NAD and ATD -- processes with which we are already familiar from our simulation experiments with coacervates. But in contrast to our models and protobions, these basic chain links in organisms (even the most primitive) are supplemented with new reactions primarily connected with the very important preparation of the substrate for its reduction-oxidation transformation. This preparation leads, on the one hand, to raising the sugar molecule to a higher energy level, which is achieved by phosphorylating the sugar by means of ATP, and, on the other hand, to decomposing the particle of hexosodiphosphate thus produced into two molecules of triosophosphate. Such a complication of the chain is an

<u>/162</u>

appreciable step forward along the road toward making energy-producing metabolism more efficient. It is interesting to note that this very ancient sequence in the conversion of matter, which underlies biological metabolism, does not require any supramolecular spatial organization, any protoplasmic structures to bring it about, but may also be simply effectuated in a homogeneous solution whose prototype is the succus saccharomyceticus expressed as far back as Buchner\*.

Therefore, the metabolic organization is here chiefly based on correlation in time of the individual reactions comprising the chain, although the precise correlation of their rates needed for this requires that advanced and specific catalysts — as only enzymes could be — are necessary to do this.

This chain of reactions leading to the transformation of glucose into pyruvate apparently possessed a very high biological refinement because, after forming at still comparatively early stages of life (perhaps about two billion years ago), it has passed through the whole evolution of living matter and has maintained itself not only in primitive microbes, but also in the metabolism of contemporary higher plants and animals.

In these two branches of living nature, which are so far removed from each other, we can observe only the bifurcation of the further transformations of pyruvate. In plants it can decompose into  ${\rm CO}_2$  and alcohol (by a type of alcoholic fermentation), but in animals it is reduced to lactate (by a type of lactic-acid fermentation).

These two types of anaerobic carbohydrate decomposition are the most common, and among many modern microorganisms they are the highroads in the evolutionary development of destructive metabolism. But in the past, of course, other variants must also have arisen, many of which were entirely rejected and destroyed by natural selection, and others were preserved until today as delicate offshoots from the main branches of the "tree of life". In actual fact, we are now discovering a large number of diverse types of anaerobic fermentation, but each of these types is proper only to a very restricted group of lower organisms. Moreover, the difference begins only with the pyruvate, but the formation of pyruvate always proceeds along the one universal path for everything alive (Figure 27).

An examination of this diagram demonstrates that, depending on the type of fermentation, other diverse fermentation products, particularly formic, acetic, propionic, succinic, butyric, and other higher fatty acids; ethyl, propyl, and butyl alcohols; acetylmethylcarbinol, acetone, gaseous hydrogen, etc. may also form in addition to alcohol, CO<sub>2</sub>, and lactic acid. It is characteristic that this diversity is achieved by incorporating a very small number of "supplementary" reactions and by continually using almost the same catalytic mechanisms. The whole matter reduces to varying the different combinations of almost always the same individual chemical events.

Of course, neither the alcohol, lactic-acid, nor other anaerobic fermentations which we have given can be regarded merely as isolated destructive processes.

<sup>\*</sup> Translator's Note: (1860-1917).



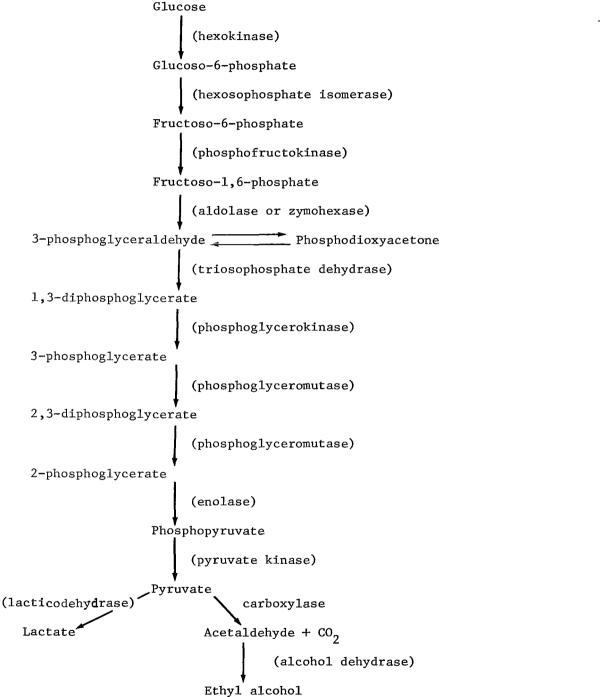


Figure 26. Diagram of Alcohol and Lactic-Acid Fermentation

They are all most intimately connected with the synthetic reactions of constructive metabolism, supplying energy and immediate structural material to them. Thus, for example, pyruvic acid, which occupies a key position in all types of fermentation, may easily be converted into one of the most important amino acids—alanine—due to ammonia and hydrogen transferred by a pyridine nucleotide in accord with the equation

Pyruvate + ammonia + 
$$NAD^{\pm}H_2$$
 = Alanine +  $NAD$  +  $H_2O$ .

The same thing may be said also of other ketonic acids. The molecular fragments resulting as intermediate products of fermentation can be condensed into long open chains, into aromatic or heterocyclic molecules acting as links for the formation of biologically important polymers.

/166

Thus, the better the individual reactions in a given type of metabolism are intercorrelated in time, the smaller the quantity of energy that is dissipated, the greater the percentage of consumable nutrient substances that goes to construct the ingredients of the system, and the more advanced biologically and more promising in evolutionary terms the system ultimately proves to be.

The interrelated metabolic paths that we have cited, however, were of course not the only possible reaction systems under the reducing conditions of the atmosphere and hydrosphere of the period in the development of terrestrial life which we are analyzing. In contemporary organisms, we may also discover other alternate routes for anaerobic conversions of organic substances. H. Krebs and H. Kornberg (Ref. 11) believe that one of these routes was the peptosophosphatic /167 cycle, the diagram of which, borrowed from their book, we give in Figure 28.

In contrast to the above-described forms of fermentation, no decomposition of a molecule of phosphorylated sugar into two molecules of triosophosphate takes place in this process, but immediately after the formation of glucoso-6-phosphate it is subjected to anaerobic oxidation, and CO<sub>2</sub> is detached from the phosphog-luconic acid thus produced, with the result that phosphoderivatives of pentoses come into being. Ribose in particular, which is very important in the building of nucleotides and nucleic acids, is formed in this fashion.

The pentosophosphate cycle is a far less universal form of carbohydrate metabolism than alcohol or lactic-acid fermentation. Only in a few microorganisms is this cycle the principal method of carbohydrate splitting; in most of them it merely supplements the ordinary forms of fermentation. Moreover, as experiments with tagged glucose show, only a small part of the sugar is split by the pentosophosphate cycle, and apparently its chief role is to form ribose.

It may be assumed that the pentosophosphate cycle had already arisen after the basic types of fermentation were organized. "It is very probable," Krebs and Kornberg write on this subject, "that the most ancient organisms did not need it. These organisms could have used the pentoses which were abundantly present in their environment. Only when the pentose content dropped substantially did the pentosophosphate cycle become organized in the organisms' metabolism." The fact that it was formed later is also indicated by the fact that the cycle, along with several reactions which have been newly produced, also includes the basic fermentation reactions. At the same time, it is very important

<sup>126 \*</sup>Note: NAD designates nicotine-amide-adenine-dinucleotide.

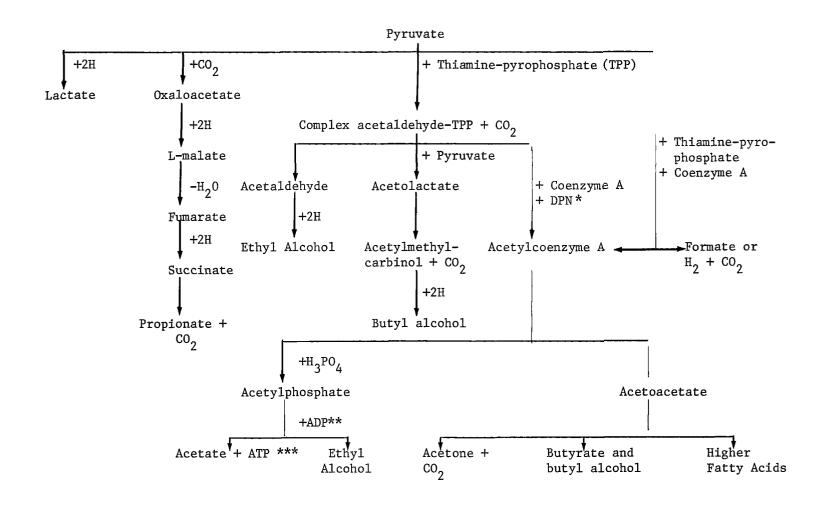


Figure 27. Principal Pyruvate Reactions in Various Types of Bacterial Fermentation \*Translator's Note: DPN designates C I.

\*\* ADP designates adenosine diphosphate

\*\*\* ATP designates adenosine triphosphate

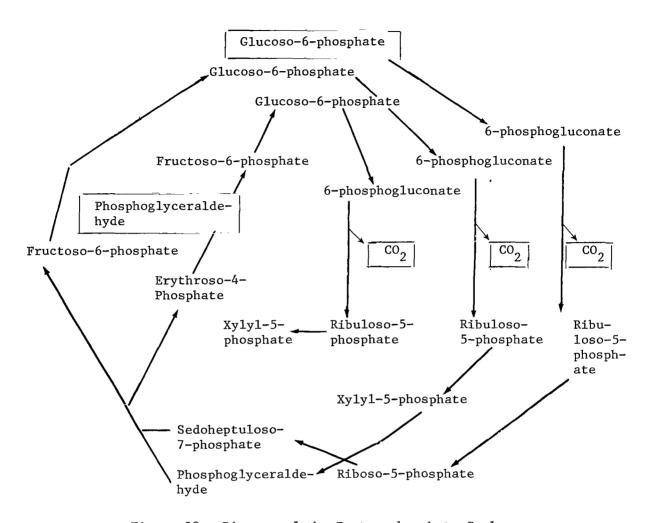


Figure 28. Diagram of the Pentosophosphate Cycle

for the following discussion to note that reactions possessing outstanding significance in photosynthesis processes appear in the pentosophosphate cycle.

The numerous forms of metabolism which we have cited characterize the variety of paths traveled by the evolution of organisms even in the absence of free oxygen in the environment, but in the presence of finished organic substances, i.e., under anaerobic and heterotrophic conditions.

The store of organic compounds contained in the "primary nutrient broth", however, must have diminished as life developed, although it was also being replenished by endogenic geological processes and meteorites and comets falling to Earth. This lent an extraordinary acerbity to the struggle for existence and was a powerful new factor in the further evolution of organisms. As these organisms developed, metabolic systems began to come into being, which allowed /168 both more efficient assimilation of the organic substances of the "primary broth" and utilization of other simpler and simpler forms of carbon nutrition

and free-energy sources of wider and wider distribution in the environment.

The early processes involving liberation and further utilization of energy were principally made up of dehydration and condensation reactions, first catalyzed by primitive catalysts and later also by enzymes. The original organisms used the surrounding medium, which was rich in organic compounds with reducing properties, for combining dehydration with the liberation and utilization of energy. As a result, the surrounding medium gradually became more and more oxidized, and its inverse reduction could take place only with expenditure of energy coming from without. An inexhaustible source of such energy was, and now is, solar radiation.

On the still lifeless Earth with its preactualistic reductive atmosphere, organic substances were photochemically transformed chiefly by shortwave ultraviolet-light energy. Ultraviolet light carries a great store of energy in each of its quanta. This same source of energy could also easily have been used by the primitive organisms in the first periods of their existence. But the gradual enrichment of the atmosphere with even small amounts of free oxygen resulted in formation of an ozone screen in it which constantly barred shortwave rays from access to the terrestrial surface. Therefore, the subsequent development of life employed longer-wave radiation, since this radiation remained accessible to organisms even in the transitional era of the Earth's existence.

The utilization of the quanta of visible light with less energy, however, demanded a very complex internal organization which could only gradually come into being and only on a comparatively high level of the development of life.

It is known that the energy of visible light may be used for effecting a number of reducing-oxidation processes in the presence of organic dyes capable of absorbing this light. A. Terenin states (Ref. 12) that the dye molecule which has absorbed light acquires a high reactive capacity enabling it to accept or deliver an electron (or hydrogen) and thus to bring about even such reducingoxidizing processes which cannot take place in the dark by themselves with no addition of light energy. The porphyrins in particular are able to play the part of this dye in organisms.

Porphyrins, whose molecule is based on a ring formed of four pyrrole com- /169 ponents, apparently originated during the evolution of organic substances at a somewhat higher stage than, for example, adenine or flavone derivatives. As the investigations of A. Krasnovskiy (Ref. 13) and A. Szutka (Ref. 14) have indicated, the synthesis of porphyrins requires free oxygen. Therefore, they could have arisen only in the transition period when the terrestrial atmosphere began to be enriched by  $0_2$  molecules.

This situation is interesting to compare with the fact that the enormous majority of modern anaerobes is devoid of porphyrins, while their needed hydrogen transfer is provided by flavin enzymes. In aerobes, on the other hand, the porphyrins play an outstanding role in the respiratory process and are the basic links in the aerobes' electron-transfer chain (Ref. 15).

Of especially great importance in this respect are the ferroporphyrins, a well-known representative of which is the red pigment of the blood -- hemin. The biological function of the ferroporphyrins (electron transfer in reducing-

oxidizing reactions) is successfully accomplished under darkness conditions with no light (Ref. 16). Here the important property of porphyrins with respect to their coloration -- the capacity to absorb light -- is consequently still unutilized.

In contrast to the ferroporphyrins, however, the metal-free porphyrins, and in particular their magnesium complexes, without possessing the properties of ordinary darkness catalysts, are capable of photocatalytic action. The work of A. Krasnovskiy (Ref. 17) and his collaborators has demonstrated that the magnesium complexes of porphyrins — bacteriochlorophyll and the chlorophyll of higher plants — as well as the metal-free porphyrins (like hematoporphyrin, for example) have the capacity for inverse reduction (acceptance of an electron or hydrogen) merely by absorbing the proper quantum of light. This photocatalytic transfer of an electron or hydrogen, unlike the darkness catalytic processes, results in an increase of the energy level of the photoreaction products — it, so to speak, "lays away in storage" part of the absorbed light energy in a very mobile, easily usable form (Ref. 18).

In the initial period of life, when the organic compounds originally produced were abundant in the external medium, visible light could not have been of decisive importance for organisms. However, as the finished exogenic organic substances were exhausted, as the short-supply of them in the surrounding solu-/170 tion increased, a greater and greater advantage in the struggle for life fell to the lot of the organisms which could utilize the porphyrins formed within them as photocatalysts. They thus were able to utilize visible light as a supplementary source of energy. This principally enabled the original colored organisms to make their heterotrophic metabolism much more efficient by making far more economical use of exogenic organic substances, without having recourse to appreciable restructuring of all their previous organization.

Ordinary heterotrophs must convert a considerable percentage of the organic substances which they derive from their environment into wastes which are no longer usable -- alcohol, organic acids, etc.

The original colored organisms, on the other hand, took advantage of the "gratis" energy of visible light for this conversion, and this freed them from inefficient expenditure of exogenic organic substances. The initial sense of photochemical reactions is found to consist just in this, and not in primary synthesis of organic substances (Ref. 19).

This may be seen from the example of a study of metabolism in present-day pigmented bacteria, in particular the *Athiorhodaceae* (Ref. 20). Externally, as regards the total balance, metabolism in these bacteria is of the ordinary heterotrophic type. They develop well in light under anaerobic conditions in solutions which must contain organic substances (e.g., butyric acid or other appropriate compounds). As the bacterial biomass grows, the quantity of exogenic organic substances in the surrounding medium correspondingly diminishes, while at the same time the bacteria give off a small quantity of carbon dioxide gas into the external atmosphere.

Their internal biochemical mechanisms are, however, substantially more complicated. They, like other organisms, are capable of securing the  ${\rm CO}_2$  of

the atmosphere. By using the elevated energy of the pigments which have absorbed light, the Athiorhodaceae here effect photocatalytic transfer of hydrogen, reducing the CO<sub>2</sub> and oxidizing the exogenic organic substances. Therefore, the formation of unutilizable wastes, which is a necessity in other heterotrophs, does not occur in them. In the light, the Athiorhodaceae utilize exogenic organic substances almost completely (90% or more) for building their biomass, while in ordinary (aphotic) heterotrophs the unusable wastes consume the lion's share of the nutrient materials (Ref. 21).

Other pigmented bacteria carry out their metabolism by the same system as do the *Athiorhodaceae*, but the hydrogen source (donor) for reducing CO<sub>2</sub> in these bacteria is hydrogen sulfide, not organic materials. This has been demonstrated/171 by the very interesting investigations by C. van Niel on purple and green sulfur bacteria (*Thiorhodaceae*) inhabiting shallow ocean inlets and lagoons rich in hydrogen sulfide which are well illuminated by the Sun (Ref. 22).

All these primitive pigmented organisms possess the type of mechanisms which make possible inverse photochemical transfer of hydrogen or an electron by the energy of absorbed light. But all of them can use only the most accessible substances as the original hydrogen source -- as, for example, organic compounds, hydrogen sulfide, molecular hydrogen, etc. (Ref. 23).

The progressive evolution of photosynthesizing organisms was directed toward producing mechanisms which would allow them to utilize a wider and wider range of substances as hydrogen donors.

This course of development inevitably resulted in incorporation of the most "difficult" -- but also the most "prevalent" -- hydrogen donor, water, into the photosynthesis reaction. In this process, the oxygen of the water had to be liberated in molecular form (Ref. 24).

Some modern organisms are interesting in that in their metabolism they have still preserved features of a more primitive organization of photosynthetic processes, but they can separate the molecular oxygen of water. They are a seemingly intermediate link between the original photosynthesizing organisms and the highly-organized photoautotrophs.

One such organism in particular is the green alga *Scenedesmus*, whose metabolism has been thoroughly studied in this respect by H. Gaffron (Ref. 25).

There is no doubt, however, that the highroad of autotrophy development was photosynthesis in the form in which we nowadays see it in the higher plants. Utilization of water as the hydrogen donor by photosynthesizing organisms was a tremendous forward step in the development of biochemical systems which combine the photostage of the process with the reaction cycles leading to gradual  $\mathrm{CO}_2$  reduction and formation of molecular oxygen.

But prolonged evolution of already rather highly developed organisms with a large armory of diverse metabolic mechanisms was required for this to happen (Ref. 26). This is substantiated by a knowledge of the photosynthetic apparatus of contemporary plants. It is exceptionally complex and, despite much research,

is still far from completely understood (Ref. 27).

For greater graphic clarity in our presentation, we will make the following comparison, which, of course, is as always extremely tentative. As an illustration, let us take any complex system performing certain work -- let us say, an automobile engine. The engine's work depends not only on its principal part, the cylinder block, but also on a number of auxiliary mechanisms, some of which are complete assemblies with their specific tasks -- preparation and delivery of the fuel mixture, production of high-voltage current to ignite this mixture, cooling, lubrication, transmission of motion, changing speed, etc.

An important factor in failure-free engine operation is not only good functioning of each of these units, but also a high degree of correlation between them, both in space and time — the timing: the spark from the spark plug must flash at a rigorously determined position of the piston in the cylinder; the mixture must arrive at the proper instant, and so on.

Similarly, in the photosynthesizing apparatus of plants we also have not only a certain chain of chemical transformations, but a series of biochemical reaction cycles, whole sets of catalytic and photochemical systems. Only when they are highly coordinated, when they continuously interact, can a reliable effect be produced. This is attained not merely from a strictly determinate combination of individual reactions in time, but also from their spatial localization, the presence of a certain structure in the photosynthesizing apparatus.

In contrast to anaerobic fermentation, (e.g., alcohol fermentation) photosynthesis cannot be simply reproduced under homogeneous conditions. It requires a definite three-dimensional organization. The need for this organization has risen to a particular height precisely because water is used as the hydrogen donor, and molecular oxygen is released in this process. In a process of this type, only separate placement of the initial unstable photosynthetic products in heterogeneous structures can prevent the probable reversal of the reaction which is thermodynamically more probable. Pigments are diffusely distributed in the protoplasm or concentrated in the surface membrane of pigmented bacteria which accomplish photosynthesis under anaerobic conditions without forming free oxygen. In contrast, the highest form of photosynthesis became possible only when specific, complexly organized structural apparatus -- plastids -- were formed during plant evolution. Electron-microscopic study of plastids indicates that they consist of colorless stroma in which "aphotic" reactions occur, and of chlorophyll-containing granules whose basic structural element is the protein-lipoid membrane. In appearance, the granules are reminiscent of stacks of coins. They consist of protein lamellae connected by a chlorophyll-containing lipoid layer (Figure 29).

Only in this sort of protein-lipoid aggregate can the initial photochemical event of water-splitting occur, but in order that photosynthesis may take place completely this event must be harmoniously combined with a long series of other processes based on enzymatic mechanisms or even on whole systems and units. Taking advantage chiefly of M. Calvin's findings (Ref. 28) we shall give a very simplified diagram (Figure 30) of the work of these units, each of which can be described by the functions which it performs in the total process of photosynthesis:



Figure 29. Electron-Microscopic Photograph of Chloroplast

(1) formation of molecular oxygen, (2) aphotic fixation of  ${\rm CO}_2$ , (3) re- /175 duction of  ${\rm CO}_2$  to carbohydrate level, (4) synthesis of sugars from phosphotriose, (5) formation of "active hydrogen" as the reduced form of pyridine-nucleotide (TPN-H<sub>2</sub>), \*(6) formation of macroergic bonds (ATP).

Light falling on the chlorophylliferous layer of the protein-lipoid aggregate knocks electrons out of it which go toward pyridine-nucleotide reduction (System 5), while the positive charges act on the water to oxidize it (System 1); the intermediate products of this oxidation are hydrogen peroxides or organic peroxides decomposing with the formation of molecular oxygen. The oxygen is principally liberated into the atmosphere, but a certain amount of it is used in System 6 for oxidative phosphorylation processes.

On the other hand, in System 2 there is aphotic CO<sub>2</sub> fixation effected principally in the same ways and by the same mechanisms (e.g., CoA), as in all other living beings. The processes occurring in System 2 result in phosphoglyceric acid which is further transformed in Systems 3 and 4 into various sugars. In System 3 it is reduced to triosophosphates (glyceraldehyde). However, this requires, first, "active hydrogen," which is delivered here as the reduced

<sup>\*</sup>In the new terminology, NADP- $\mathrm{H}_2$  is an NAD- $\mathrm{H}_2$  analog containing not two, but three particles of phosphoric acid.

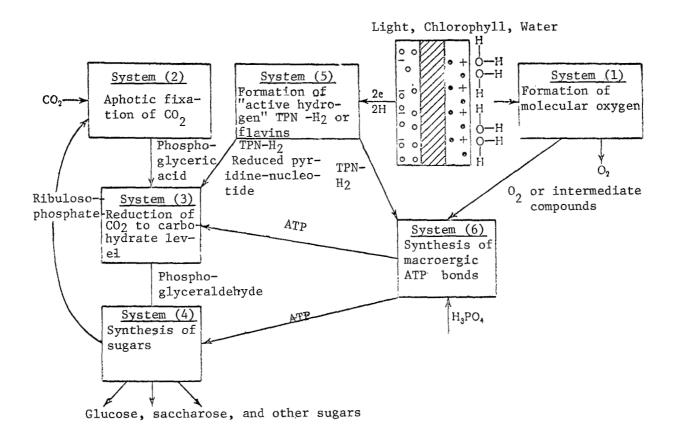


Figure 30. Diagram of Interaction of Separate Units in Photosynthesis Process

pyridine-nucleotide (TPN-H<sub>2</sub>) from System 5, and, second, an easily available source of energy (ATP) produced by System 6.

System 4 further transforms the triosophosphates. This is done either by simply condensing them (with concomitant formation of hexosodiphosphate and then glucose) or by converting them in a more complex fashion, resulting in the formation of phosphoric esters of all monosaccharids with 4, 5, 6, 7, and 10 carbon atoms which are intrinsic to the plant kingdom. In particular, the phosphoric ester of pentose is formed here — ribulose, a substance which, as we saw above, is a characteristic intermediate product of the pentosophosphate fermentation cycle. Ribulosomonophosphate plays a very important role in photosynthesis, since after additional phosphorylation by ATP it enters System 4, where it serves as the primary CO<sub>2</sub> acceptor during its aphotic fixation.

A detailed knowledge of the photosynthesis apparatus in green plants shows that all its catalytic mechanisms, and even whole aggregates of them, represent /176 nothing fundamentally new. In most cases, we also find the same or similar mechanisms in different colorless organisms or in bacteria which photosynthesize.

Therefore, even before the appearance of green plants, before the development of modern forms of photosynthesis these chemical mechanisms existed, but they were not united into a single complex sustem. It was just this unification of pre-existing "mechanisms" which occurred in the development of the photosynthetic apparatus. It could be formed during the evolution of organisms only on the foundation of already existing systems and reactions.

The rise of photosynthesis was an extraordinarily important stage in the evolutionary process of the organic world on our planet. It radically altered all previously existing relationships and caused the preactualistic era in the Earth's existence to change into the actualistic era, when free oxygen began to accumulate rapidly in the atmosphere.

For modern anaerobes, oxygen is a harmful gas, greatly inhibiting their growth and depressing their development. The reasons for this are still not completely clear -- they apparently may vary in the different anaerobes. Most of them are capable of absorbing atmospheric oxygen, probably because flavins -- which are the principal hydrogen carriers in anaerobic oxidoreduction -- are auto-oxidizable substances, compounds capable of direct oxidation by molecular oxygen (Ref. 29). In the absence of free oxygen, this has no significance for anaerobic metabolism. When O<sub>2</sub> appears, this metabolism is disturbed, perhaps because of destruction of the flavin mechanisms or the formation of hydrogen peroxide, which in aerobes decomposes the ferroporphyrins which are lacking in

Primitive anaerobes.

However that may be, during the period that free oxygen appeared and gradually increased in the environment, the struggle began to maintain anaerobic conditions of life, and in this struggle those organisms survived which somehow

adapted to the advancing change. This was attained not only by direct with-drawal from immediate contact with the atmosphere, but also by a gradual change in the nature of metabolism, which varies in the diverse representatives of the

In this transition period, metabolism was also organized in such a unique group of organisms as the chemoautotrophs. Right on the borderline between reducing and oxidizing conditions, the widest possibilities were created in principle for oxidation of reduced inorganic compounds of the terrestrial crust by molecular oxygen.

In the period of initial formation of free oxygen which we are examining, these oxidizing reactions must have been occurring literally at any point on the Earth's surface, since there were substrates everywhere capable of oxidation. However, abiogenically these reactions proceeded very slowly, and the energy liberated because of them was lost and scattered as heat.

Under conditions of acute scarcity of exogenic organic compounds, the organisms which in their evolutional development could incorporate these reactions of inorganic substance oxidation into their own metabolism, and in their own bodies formed catalytic mechanisms accelerating these processes and mobilizing their energy for biosyntheses, acquired great advantages in the struggle for existence. The advantages were therefore reinforced by natural selection and subsequently began to develop extensively.

Today, we as a rule find organisms capable of a chemoautotrophic mode of life under natural conditions right where reduced substances from the interior, coming to the surface of the Earth, encounter the molecular oxygen of the atmosphere (Ref. 31).

Therefore, the modern role of chemoautotrophs in the cycle of matter is very great. In practice, under natural conditions all oxidation processes of reduced compounds of nitrogen and sulfur, as well as hydrogen, methane, and iron (in part) involve the vital activity of the corresponding microorganisms (Ref. 32). The great systematic variation of the chemoautograph group and the closeness of some of its representatives to diverse groups of heterotrophs whose metabolism is more primitive (with many of the chemoautotrophs being linked to these heterotrophs by transitional organisms) convinces us that chemoautotrophy took place repeatedly. However, the start of its most luxuriant development goes back to a time when there was already a great variety of organic forms (Ref. 33).

This development was favored by specific conditions of the period which we are discussing — principally the insufficiency of organic nutriment and the great store of inorganic energy sources. However, when the Earth's surface changed to oxidizing conditions this reserve was rather rapidly expended, and replenishment of it from the deep layers of the Earth's envelope took place comparatively slowly. On the other hand, the balance of organic substances in the biosphere became more and more positive because of the formation and rapid development of photoautotrophs.

/178

136

This permitted the main evolutionary stream to return to the old channel of the further development of organisms adapted to feeding on organic substances. The period of an acute lack of these substances was left behind, and a small group of autotrophic organisms capable of chemosynthesis and representing only lateral branchings from the main evolutionary stream was preserved merely as a biological memory of it. The main channels of this stream were now the green photoautotrophic plants and the colorless organisms maintaining the former more ancient method of heterotrophic nutrition. After the rise of photosynthesis, the evolution of these organisms which used finished organic substances in their vital processes now began to occur on entirely different biochemical bases. decisive condition in this regard was the atmospheric oxygen, the presence of which made possible a substantial advance in the efficiency and intensity with which the energy of organic substances was mobilized. It is understandable that this increase in efficiency took place on the basis of the same anaerobic mechanisms which had earlier supported the energy-producing metabolism of the ancient heterotrophs.

During evolution under the new aerobic conditions, however, natural selection preserved and reinforced for further development precisely those organisms in which supplementary enzyme complexes and reaction systems had originated, allowing them to obtain far more macroergs than formerly from exogenic organic substances by complete oxidation of these substances with atmospheric oxygen (Ref. 34).

The solution of this problem demanded that two new systems come into being: first, a system for mobilizing the hydrogen which under anaerobic conditions was not used and was given off by the organisms in the form of reduced organic compounds which were no longer usable (acids, alcohols, etc.), or even as gaseous hydrogen; and, second, a system for activating oxygen so as to oxidize hydrogen into water and to effectuate the oxyhydrogen reaction.

Individual mechanisms of the first system are very ancient. They were principally inherent in anaerobic organisms. They are our familiar NAD, ATP, CoA, etc., but their action when aerobiosis came into being spread to a number of new products lacking in the chain of alcohol or lactic-acid fermentation. This chain of initial carbohydrate transformation also remained unchanged in the aerobes, but at certain locations they added to it new chains and reaction cycles whose individual members give up their hydrogen to NAD or other similar acceptors (e.g., flavin derivatives).

<u>/180</u>

These locations for attachment of new cycles were distinctly marked even in the rather primitive facultative anaerobes. The main one was pyruvic acid, that key point from which the roads of different forms of anaerobic fermentation spread in different directions (Ref. 35). In Streptococcus faecalis, for example, pyruvic acid by oxidative decarboxylation is thus converted into acetic acid; in contrast to this, in bacteria of propionate fermentation it attaches CO<sub>2</sub> to itself and forms oxaloacetic acid. Both these processes of converting pyruvic acid which has formed in the usual way take place in higher organisms capable of respiration. However, the matter does not stop here, but a multi-link, closed chain of transformations arises. This chain has been given the name of Krebs cycle (Ref. 36), or the di- and tricarboxylic acid cycle (Figure 31). For

purposes of simplicity, the diagram does not show the anaerobic method of

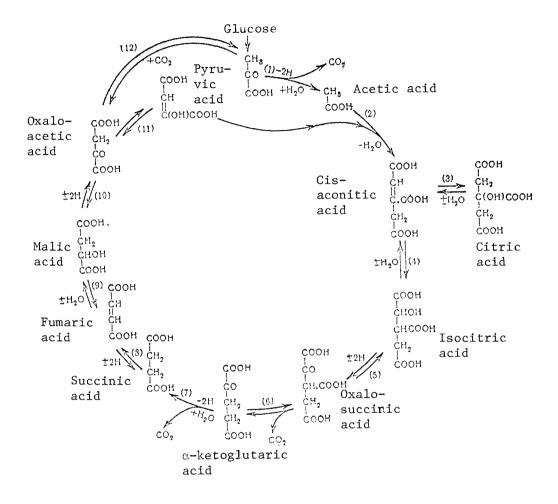


Figure 31. Krebs Cycle

converting glucose into pyruvic acid which is usual in all organisms. Without dwelling in detail on all the links in this complex cycle in which many mechanisms already familiar to us participate, we must mention the following.

When passing through this cycle, all three carbon atoms of the pyruvic acid molecule are oxidized into acetic acid due to oxygen in the water, while the hydrogen is continually eliminated from the cycle by means of the NAD and corresponding enzymes -- the oxidoreductases. The acetic acid is directly split by carboxylases, whose composition includes thiamine-pyrophosphate (TPP).

We thus see that the same classes of enzymatic mechanisms are operating here as in anaerobic metabolism, but the order of the reactions is now essentially changed. The principal difference is that the liberated hydrogen does not fall into discard, but is utilized to produce significant additional quantities of energy by undergoing oxidation with atmospheric oxygen. The intermediate products generated in the cycle combine it with other systems of metabolism, with the result that there is established an immediate relationship and reciprocal state of interdependence between the metabolism of carbohydrates, fats, organic acids, and proteins. In particular, for example, the ketonic acids generated in the cycle by direct interaction with ammonia — i.e., by direct amination or reamination reactions — are converted into alanine, aspartic acid, and glutamic acid, while various other amino acids participating in the system of proteins, hormones, enzymes, etc. are also formed from them (Ref. 37).

/181

Additional respirational transformations may be added to the fermentation reaction chain not only by means of the pyruvic acid at the end of this chain, but also by means of its initial links.

In this case, respiration is linked to the pentosophosphate cycle which in modern organisms is chiefly represented in this aerobic form.

Hydrogen removal by NAD from the intermediate links of the Krebs cycle does not involve liberation of a perceptible amount of energy. The free energy of oxidation becomes accessible not in oxidation of the substrate, but in subsequent oxidation of NAD-H<sub>2</sub> by atmospheric oxygen. This takes place not in a single event, but by the transfer of protons and electrons through the chain of a number of specific oxidizing enzymes. As the result of this transfer, each of the intermediate carriers, present in very small quantity, is continually reduced by the substrate and is oxidized by molecular oxygen. The phosphorylation which is usually called oxidative phosphorylation (Ref. 38) is associated with this type of oxidation in which oxygen participates. Oxidative phosphorylation is a very significant, essentially the chief source of free energy for acorbic organisms. In actual fact, it has now been established that oxidation of merely a single molecule of NAD forms three pyrophosphate bonds (ATP), while fermentation of a whole sugar molecule brings about only two such macroergic bonds.

Rather diverse substances (mediators) may be the intermediate links in the oxidation chain in various organisms, but the prinicpal role here belongs to the flavoproteides. As G. Mahler has indicated (Ref. 39), a great variety of compounds of this type can be detected in different representatives of the animate world. In several of them, the flavone group can combine with nucleotides and other organic radicals, as well as with such metals as iron,

molybdenum, or copper.

In some cases the flavin enzymes receive hydrogen from the reduced NAD and transmit it to porphyrins -- the components of the cytochrome system -- or else to other intermediate oxidizing mechanisms which perform final oxidation of this hydrogen by atmospheric oxygen. In other cases, such flavoproteides participate as can derive hydrogen directly from the substrate and transmit it to the cytochrome system. Finally, there are flavoproteides capable of transferring the hydrogen which they obtain directly to the molecular oxygen.

/182

The great variety of the reaction sequence in the oxidative chain in various representatives of the animal and plant kingdoms indicates the relative youth of the system which we are analyzing. It also indicates that, in the course of evolution, it had originated in parallel fashion in different organisms at the development stage of the animate world where profound differentiation between its individual parts took place.

We may arrive at similar conclusions from a knowledge of the diverse enzymes participating in the oxidative transformation chain in various organisms. This refers particularly to the "terminal group" of these catalysts which directly activate molecular oxygen (Figure 40). In organisms which are far apart in the systematic respect, this problem is frequently solved by very different catalytic mechanisms. Along with the most ancient flavin enzymes, we must here mention the cytochromes which we have been able to detect even in rather primitive aerobic organisms. With the appearance of molecular oxygen in the terrestrial atmosphere, the cytochromes contained in the most diverse living beings could very easily have begun to function as oxidasic mechanisms activating oxygen in the respiration process.

Therefore, cytochromes and the corresponding enzymes — cytochromoxidases — are rather universal respiratory devices. We find them in groups of organisms which are very disparate in the systematic respect, but their significance is particularly great in the respiratory process in several microorganisms, as well as in the animal cell. In higher plants, a large role falls to the phenoloxidase systems in which the enzymes are proteides, and the hydrogen carrier is represented by Palladin's "respiratory chromogens" (Ref. 41). These mechanisms are very specific to plants. Apparently during phylogenesis they had already taken form when the separation of organisms into the plant and animal kingdoms took place.

Of very great importance in plant respiration is also peroxidase, which activates the oxygen of hydrogen peroxide, but in the animal cell it plays a comparatively small role. Besides cytochromoxidase, phenoloxidases, peroxidases, and flavin enzymes, the mechanisms of ascorbinoxidase lipoxidase, and many others can catalyze "final" oxidation by atmospheric air.

In various living beings and at different stages in their life cycle, the /183 role of these individual mechanisms may fluctuate widely. All this indicates the comparative phylogenetic youth of the respiration process and that it took shape considerably later than the anaerobic method of energy-producing metabolism.

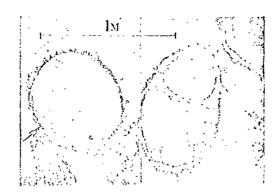


Figure 32. Protein-Lipoid Membrane of Bacterium *Micrococcus Lysodeikticus* 

The great complexity of the spatial organization of protoplasm needed for respiration also leads us to the same conclusion. While fermentation and the anaerobic phosphorylation associated with it may occur even in homogeneous solutions, the mechanisms of respiration and oxidative phosphorylation are closely related to specific structures in living bodies. Attempts to realize these processes simply in a solution of the appropriate enzymes and mediators have always ended in failure. Obviously, successful transmission of protons and electrons along the chain of oxidative systems requires that they be accurately localized with respect to each other in space, otherwise the chain is ruptured at some link. Particularly sensitive in this respect is the relationship between oxidation proper and phosphorylation. Thus, for example, when certain concentrations of specific inhibitors are used, "respiration" proper may still be maintained, but it is irreparably "disengaged" from phosphorylation.

The most primitive structural formation, which we can detect even in Goldacre's vesicles or on the surface of Bungenberg-de-Yong's coacervate droplets, is the protein-lipoid membrane. A similar sort of membrane may also be found on the surface of a number of bacteria. If they are subjected to lysis, these membranes may be isolated as so-called ghosts. The investigations by N. Gel'man (Ref. 42) on bacteria which are rather primitive, but capable of respiration, indicated that in these bacteria the enzymes of the electron-trans-/184 fer chain are also incorporated into their surface protein-lipoid membranes (Figure 32). Thus, respiration as a whole can occur only when this sort of spatial "assembly" of the enzymes is kept undisturbed.

The three-dimensional organization of respiration has reached even more appreciable complexity and perfection in the higher organisms of the present day.

Here the function of respiration is accomplished by structural formations specifically adapted to that end -- the mitochondria (Figure 33) (Ref. 43). Their very delicate internal structure, which can be observed only under the electron-microscope, is basically characterized by the presence of a very elaborate system of protein-lipoid membranes, in a certain degree similar to the

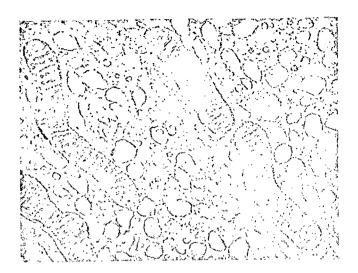


Figure 33. Electron-Microscopic Photograph of Mitochondria of Murine Epididymus

situation we noted above for chlorophylliferous granules. Therefore, the system of protein-lipoid membranes may be regarded as a very general principle of spatial organization in living bodies.

Due to the rigorously determinate mutual arrangement of the enzyme complexes on the ultrafine structure of the mitochondria, the whole apparatus taken together attains an exceptional functional refinement. In particular,  $\frac{185}{185}$  for example, the great perfection of the electron transfer process in the system of flavoproteins and hemin enzymes in the mitochondria, says D. Green (Ref. 44), depends on the contact made here between the indicated enzyme groups and the lipoproteide membranes.

The mitochondria of contemporary higher organisms, like the chloroplasts of plants, are very complex and refined devices well adapted to perform definite biological functions.

Obviously these devices can originate only after the very lengthy development of living beings as they advanced toward perfecting their aerobic metabolism, considerably after the formation of the bulk of the oxygen in the Earth's atmosphere. This is also indicated in particular by the fact that mitochondrial structure can exist only at a relatively high partial  $\boldsymbol{0}_2$  pressure. The research of P. Gavodan et al. [no ref.] has shown that mitochondria vacuolize and disintegrate if the oxygen content of the environment becomes less than 30% of its usual norm.

We, unfortunately, do not yet have at our disposal data which would help us form a concept of the path followed by subsequent mitochondria formation from

more primitive protoplasmic structures during the evolutional development of organisms.

In even greater measure this may be said about another very important cellular structure -- the cell nucleus.

The intramolecular structure of DNA, originating at some time in the past on the basis of separation and rationalization of nucleic acid functions, must, of course, have had a protracted evolution during the development of life. This structure became more and more adapted toward solving the problem of the most precise self-reproduction and transmission of hereditary information. However, a very important role in this regard must also have been played by development of the multimolecular structures which were formed with the predominant participation of DNA. This was particularly important for solving the problem of uniform DNA distribution in the process of cell division.

In bacteria and blue-green algae we find a spatial organization which is still on a relatively low level of development. Here, contrary to the situation in more highly organized cells, the nuclear substance is simply located in the center of the protoplast in the form of spherical or twisted structures con- /186 sisting of DNA and having chemical properties characteristic of the nucleus. The structures of these formations do not, however, correspond to the typical cell nuclei of higher organisms, since they evince none of the internal structural differentiation inherent in the latter, nor are they delimited by a distinct membrane from the protoplasm surrounding them. When the cells of bacteria and blue-green algae divide, there is probably a simple separation of the nuclear matter into two daughter fragments.

The role of the internal nuclear structure has undergone exceptionally great growth because of the phenomenon of cellular copulation, especially because of the sexual process. After the development of the latter, the problem of the proper distribution of the nuclear substance became immeasurably complicated. This also led to the formation of a new organization — quite astonishing in its fineness and precision — of the nucleus capable of mitosis. This organization could, of course, have become complicated only in the course of subsequent, very prolonged evolution of organisms on a rather high level of development.

Therefore, the evolutionary development of the cell in its modern form, the cell which we ordinarily consider the most primitive indivisible element of life, demanded gigantic periods of time for its realization, a succession of numberless generations of precellular living beings. Some modern authors (Ref. 45), resurrecting the old theory of S. Merezhkovskiy about symbiogenesis (Ref. 46), even believe it possible that in the initial periods of life separate structural formations were developed as independent protobions or primitive organisms, and only thereafter did they combine into that most complex biological assemblage which is the cell.

The formation of the organization in time and space which is characteristic of all contemporary living creatures, the formation of the bases of biological metabolism and of cellular structure, can be understood only by studying the evolutional history of life and the establishment of biological laws specific

to that evolution.

Many, many hundreds of millions of years, perhaps half the time during which life has existed on Earth, was required for the formation of those bases during the evolution of life.

Therefore, attempts to reproduce directly and articicially, to synthesize even the most primitive modern living being now still seem very naive. The synthesis of life must obviously begin with the same systems which were the initial ones during the development of life among us on Earth.

<u>/187</u>

The metabolism of living bodies and the very fine structure which is characteristic of them result in a number of properties which are obligatory for any living being we now know, properties which in their totality qualitatively differentiate organisms from objects of the inorganic world. This is the capacity of living bodies for active selective absorption of substances from their environment and for excretion of metabolic products back into that medium. This also includes the capacity to grow, multiply, reproduce oneself, move in space, and, finally, that reaction which is characteristic of everything alive — the response of organisms to external action, their ability to be stimulated.

Each of these properties during the subsequent development of organisms not only became more and more complex, but also was transformed into qualitatively new forms of life.

Since the evolution of life has already flowed not through a single channel alone, but has taken place over numerous branching roads, these new forms have proved to be characteristic not of the whole world, but merely of a certain portion of it, but we must never ignore them if we wish to form a really comprehensive concept of life.

The farther the evolution of living beings has gone, the more these new forms of life have taken on a complex and biologically mediated nature. Therefore, they cannot be mechanically reduced to elementary processes of inorganic nature by bypassing the evolutionary course followed by the development of living matter. Actual understanding of them can be achieved only on this course when we study the history of their development from more primitive forms of biological organization.

## REFERENCES

- 1. Zuckercandle, E., Pauling, L. Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry). Izdatel'stvo "Nauka,", p. 54, 1964.
- 2. Evolyutsionnaya biokhimiya. Trudy V Mezhdunarodnogo biokhimicheskogo kongressa. Simpozium III (Evolutionary Biochemistry. Transactions of the Fifth International Biochemical Congress. Symposium III). Izdatel' stvo AN SSSR, 1962; The Evolution of Life, V. I Evolution after Darwin. University of Chicago Press, 1960.
- 3. Florkin, M. Biochemical Evolution. Acad. Press, 1949. Comparative Biochemistry, ed. by M. Florkin and H. Meson, Acad. Press, 1949.
- 4. Cohen, S. On Biochemical Variability and Innovation. Woods Hole, Mass.

Library of the Marine Biological Laboratory, 1962. Advance Virus Res., Vol. III. Acad. Press, 1955.

5. Ternetz, Ch. Jahrb. Wiss. Bot., 51, 435, 1912.

非正式的には、 との様によったとうことをことがする

6. Artari, A. K voprosu o vliyanii sredy na formu i razvitiye vodorosley (On the Problem of the Effect of Environment on Form and Development of Algae). Moscow, 1903; Harder, R. Zschr. Bot., 9, 145, 1917; Skinner, C., Gardner, C. J. Bact. 19, 161, 1930; Goryunova, S. Khimicheskiy sostav i prizhiznennyye vydeleniya sine-zelenykh vodorosley (Chemical Composition nd Discharges During the Life of Blue-Green Algae). Izdatel'stvo Akademii Nauk SSSR, 1950.

- 7. Obel', Ye. Vozniknoveniye zhizni na Zemle (In the Book: Origin of Life on Earth). Izdatel'stvo Akademii Nauk SSSR, N, 585, 1959.
- 8. Ehrensvard, G. Ann. Rev. Biochem., 24, 275, 1955; Davidson, J. The Biochemistry of the Nucleic Acids. London, Methuen, 1953.
- 9. Tauson, V. Priroda, 6, 43, 1934; Osnovnyye polozheniya rastitel'noy bio-energetiki (Basic Theses of Plant Bioenergetics). Izdatel'stvo Akademii Nauk SSSR, 1950; Zobell, C. Adv. Enzymol., 10, 443, 1950.
- 10. Thaysen, A. Proc. Third Internat. Congr. Microbiol., p. 729, 1940; Rosenfeld, W. J. Bacteriol., 54, 664, 1947.
- 11. Krebs, H., Kornberg, A. Energy Conversion in Living Systems. Izdatel' stvo Inostrnnoy Literatury, Moscow, 1959.
- 12. Terenin, A. Photokhimiya krasiteley (Photochemistry of Dyes). Izdatel' stvo Akademii Nauk SSSR, 1947.
- 13. Krasnovskiy, A., Umrikhina, A. Doklady Akademii Nauk SSSR, 155, 691, 1964.
- 14. Szutka, A. The Origin of Prebiological Systems. Acad. Press, 1965.
- 15. Dolin, M. The Bacteria, V. 11, p. 425, Academ. Press, 1961.
- 16. Krasnovskiy, A. Doklady Akademii Nauk SSSR, 60, 421, 1948; 103, 283, 1955.
- 17. Krasnovskiy, A. Zhurnal Fizicheskoy Khimii, 30, 968, 1956.
- 18. Krasnovskiy, A. Izvestiya Akademii Nauk SSSR, Seriya Biologicheskaya, 2, 122, 1955.
- 19. Kondrat'yeva, Ye. Fotosinteziruyushchiye bakterii (Photosynthesizing Bacteria). Izdatel'stvo Akademii Nauk SSSR, 1963.
- 20. Muller, F. Arch. Microbiol. 4, 131, 1933.
- 21. Foster, I. J. Bacterial, 47, 355, 1944. Bacterial. Physiology, ed. C. Werkman and P. Wilson, p. 361, Acad. Press, 1951.
- 22. van Niel, C. Arch. Microbiol., 3, 1, 1931; 7, 323, 1936.
- 23. van Niel, C. Photosynthesis in Plants, ed. Y. Franck and W. Loomis, p. 437, 1949.
- 24. Arnon, D. Trudy V Mezhdunarodnogo biokhimicheskogo kongressa. Simpozium VI (Proceedings of the Fifth International Biochemical Congress. Symposium 6). Izdatel'stvo Akademii Nauk SSSR, 1962.
- 25. Gaffron, H. Amer. J. Bot., 27, 273, 1940. Plant. Physiology, ed. F. Steward, Acad. Press, 1960.
- 26. Gaffron, H. Gorizonty biokhimii (In the Collection: Horizons of Biochemistry). Izdatel'stvo "Mir", p. 49, 1964.
- 27. Rabinovich, Ye. Fotosintez (Photosynthesis). Izdatel'stvo Inostrannoy Literatury, 1951-1953.
- 28. Calvin, M. Conférences et Rapports, 3-ème Congrés International de Biochimie (Conferences and Reports, 3rd International Congress of Biochemistry). Bruxelles 1-6 August 1955, p. 211, Liège, 1956.
- Oparin, A., Kharat'yan, Ye., Gel'man, N. Doklady Akademii Nauk SSSR, 157, 207, 1964.

/188

- 30. MacElroy, W., Seliger, G. Trudy V Mezhdunarodnogo biokhimicheskogo kongressa. Simpozium III (Transactions of the Fifth International Biochemical Congress. Symposium III). Izdatel'stvo Akademii Nauk SSSR, p. 161, 1962.
- 31. Isachenko, B. Mikrobiologiya, 4, 964, 1937.
- 32. Kuznetsov, S. Mikrobiologiya, 17, 307, 1948.
- 33. Sorokin, Yu. Dissertatsiya (Dissertation), 1954. Trudy V Mezhdunarodnogo biokhimicheskogo kongressa. Simpozium III (Transactions of the Fifth International Biochemical Congress. Symposium III). Izdatel'stvo Akademii Nauk SSSR, p. 175, 1962.
- 34. Khorekker, B. Ibid., p. 91.
- 35. Bernhauer, K. Erg. d. Enzymforsch., 3, 185, 1934.
- 36. Krebs, H. Sympos. sur le Cycle Tricarboxylique (Symposium on the Tricarboxylic Cycle). Second International Congress of Biochemistry, p. 42. Paris, 1952.
- 37. Braunshteyn, A. 12-e Bakhovskoye chteniye (Twelfth Bakh Lecture). Izdatel' stvo Akademii Nauk SSSR, 1957.
- 38. Kotel'nikova, A. Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry).

  Izdatel'stvo "Nauka", p. 80, 1964; Skulachev, V. Uspekhi Biologicheskoy Khimii, Vol. 6. Izdatel'stvo "Nauka", p. 180, 1964.
- 39. Mahler, G. Conférences et Rapports de 3-ème Congrès International de Bio-/189 chimie (Conferences and Reports of the Third International Congress of Biochemistry), p. 264. Bruxelles, Liège, 1956.
- 40. Mikhlin, D. Biokhimiya kletochnogo dykhaniya (The Biochemistry of Cellular Respiration). Izdatel'stvo Akademii Nauk SSSR, 1960.
- 41. Oparin, A. Biochem. Zeit., 282, 155, 1927.
- 42. Gel'man, N. Uspekhi sovetskoy biologii, 47, 152, 1959; Problemy evolyutsionnoy i tekhnicheskoy biokhimii (In the Collection: Problems in Evolutional and Technical Biochemistry). Izdatel'stvo AN SSSR, p. 159, 1964.
- 43. Lehninger, A. The Mitochondrion. Publisher, Benjamin N.Y., 1964.
- 44. Green, D. Trudy V Mezhdunarodnogo biokhimicheskogo kongressa. Plenarnyy doklad (Transactions of the Fifth International Biochemical Congress. Plenary Report). Izdatel'stvo Akademii Nauk SSSR, 1962; Gorizonty biokhimii (In the Collection: Horizons of Biochemistry). Izdatel'stvo "Mir", p. 293, 1964.
- 45. Ris, H., Plant, W. J. Cell. Biol., 13, 383, 1962.
- 46. Merezhkovskiy, S. Biol. Zbl., 30, 278, 321, 353, 1910.

CONCLUSION

/190

· .

In conclusion, we will endeavor to give an objective chronology of the events described above, since without it the history of the development of life on Earth cannot be complete.

At the present time, however, we may speak (and even then rather tentatively) only of the sequence of the separate stages of biogenesis, but absolute data established by studying palaeontological finds refer principally to much later events in the development of life on Earth.

If we start counting the age of our planet from the time when it began to form from the material of the protoplanetary cloud, we can assume this age to be about 5,000,000,000 years in round numbers. Therefore, if we wanted to present the whole history of the Earth, we would have to write ten volumes of five hundred pages each, where every page would correspond to a period of a million years. Not long ago it was believed that we could read only one volume of this history, the tenth and last.

Fossil remains of animals and plants preserved from the beginning of the Cambrian period enable us to visualize clearly the irreversible process of the consecutive development of the organic world which has been uninterruptedly going on for 500,000,000 years. The separate major stages which have succeeded each other in this long course of the development of life are so distinctly represented in the palaeontological chronicle of the Earth for this period that the entire process as a whole may serve as a reliable chronometer with which /191 geologists may determine the time at which the sedimentary rocks which they have studied were formed.

Thumbing successively through the pages of this volume and studying the chronology of the major events with which the developmental history of the organic world in the last 500 million years has been so rich, we find that the rate of this development has steadily increased. At the beginning of the period under discussion, this rate was rather low, considerably slower than at the end. It took almost half of this period, for example, for plants to conquer the dry land completely and for amphibious animals, still retaining their complete dependence on the water, to crawl upon the shores of seas and swamps.

Subsequent development of the terrestrial world of animals took place appreciably faster, but still about a hundred million years had passed before the reign of the reptiles, which reached its apogee only sixty or seventy million years ago, was established on Earth. Only half of this time, the next thirty-five million years, was required before the empire of the reptilians was replaced by that of birds and animals, which then assumed the features quite familiar to us now only some five to seven million years ago. And only the single final page of our volume encompasses the whole history of mankind.

The high, and still rising, rates of development of life in this period of time have caused the striking variety of the world of highly organized plants and animals surrounding us. But the beginning of life, of course, in no way coincides with the beginning of our tenth volume. On the contrary, even in its very first pages we encounter rather lush development of life with a great number of species of multicellular algae and diverse invertebrates: medusas, worms, echinoderms, mollusks, and trilobites. Only vertebrates are missing here.

In the plants and animals we have listed, however, there are already comparatively highly organized living beings which could have originated only from the very protracted development of life which preceded the Cambrian period.

Even comparatively recently it was believed that the palaeontological chronicle broke off at the Cambrian period, that remains of organisms which inhabited the world more than half a billion years ago had not been preserved to

147

our time, since the rocks containing them had undergone profound changes and metamorphosis, completely destroying all biological structures. However, we have recently determined that at many spots on Earth, particularly on continental plateaus, like the Russian, Siberian, and Sino-Tibetan, below the layers with the most ancient complexes of Cambrian fossils there are strata of very slightly altered rock closely associated with the overlying layers, which are at times quite thick. They lie under Cambrian deposits and form a unified whole with them.

<u>/192</u>

In different parts of the globe, these strata have been given different names (Sinisian, Eocambrian, Beltian, etc.). In the USSR, at the suggestion of N. Shatskiy, they are set apart in the so-called Riphean, now assigned to the Proterozoic Era.

A study of these rocks began comparatively recently, but we have now already discovered in them numerous fossils preserved from the Pre-Cambrian organic world (Ref. 1).

These investigations show that late Pre-Cambrian life was a direct pre-decessor of the Cambrian. The fossils discovered here indicate that rather rich florae and fauna, represented by comparatively highly-developed organisms, both unicellular and multicellular, existed at that time.

In the coaly shales of the Breton Pre-Cambrian, for example, remains have been found of radilarians, foraminifera, and siliceous sponges. In the Pre-Cambrian of the Grand Canyon of North America, G. Walcott found remains of polychaetous worms. In Sweden imprints have been found of an arthropod, perhaps the progenitor of the Cambrian trilobites. In the Pre-Cambrian of the USSR and China, A. Vologdin (Ref. 2) found the siliceous sponges which are most primitive in terms of spicule structure, imprints of worms which later in the Cambrian became more developed, and other traces of the animal life of the late Proterozoic.

In deeper layers, however, animal remains are completely absent, perhaps because the primitive animals of that time were unable to form skeletons or shells, and their soft bodies have disappeared without a trace in the gigantic periods of time which separate us from the Pre-Cambrian.

In contrast to this, the plant world is represented in these rocks by numerous fragments and accumulations of various algae and the spores of primitive plants (Figure 34) (Ref. 3). Therefore, the epoch of life, the Proterozoic Era, preceding the Cambrian, rises before our eyes. This era was an immense stage in geological development, and began almost two billion years ago, i.e., in that exceptionally important period in life on the Earth's surface when the atmosphere of our planet began to lose its reductive nature and gradually became enriched with free oxygen.

<u>/193</u>

This gigantic era, exceeding in length more than twice all succeeding eras taken together, is usually divided into three geologopalaeontological systems:

(1) The Sinisian, which began about 1200 million years ago and lasted until the Cambrian;

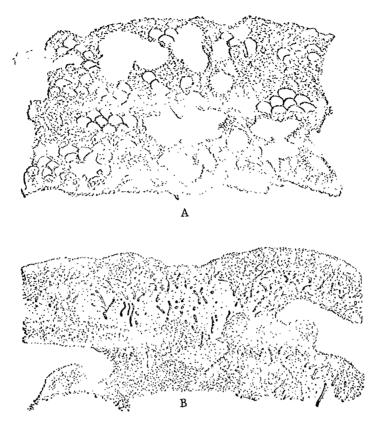


Figure 34. Fossils of the Alga (A) Somellostroma visiculare\* Vologdin and (B) Pralarenaria bullulata Vologdin. Lower Cambrian.

- (2) the Yenisei (or Yeniseian), which began 1500 million years ago and ended 1200 million years ago;
- (3) the Sayan or (Sayanian), which began 1900 and ended 1500 million years  $\frac{194}{2}$  ago.

The Sinisian period alone thus encompasses the whole ninth and the second half of the eighth volume of our history of the Earth; the Yenisei system occupies the beginning of the eighth volume; the greater part of volume seven is covered by the Sayan system.

Many pages in these volumes have, unfortunately, suffered from the ravages of time; many are completely lost, and the order of others is greatly confused and distorted. In a number of cases, in particular, it has had to be admitted that Riphean rock strata sometimes contain plant fragments and spores of considerably younger age than would follow from the geological data of their

<sup>\*</sup>Translator's Note: This is probably a typographical error and should be vesiculare.

locality. They were obviously brought at some time in the past to that place from upper layers. Therefore, special care must be exercised in approaching any sort of random -- unsystematic -- finds in a stratum of Riphean or even older rocks.

We are, nevertheless, now already able to describe the development of life in the Proterozoic Era, although still in a very general and approximate manner. We do not find here the splendid variety of modern organic forms and that rapid replacement of them in time which is characteristic of the tenth volume of the history of the Earth. It may be thought that the evolution of life in that era flowed along at less tempestuous rates than in the periods subsequent to the Cambrian.

The Proterozoic is principally an era of algae and bacteria (Ref. 4). As we have seen, the most primitive representatives of multicellular animals appeared only at the end of it. It may, of course, be assumed that even at earlier periods there were unicellular animals, especially protozoans, but in this regard we have almost no factual material at our disposal. In contrast to this, the plant world of the Proterozoic era has left behind numerous and completely reliable remains.

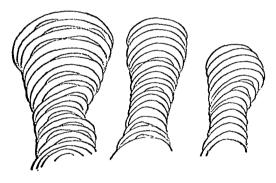


Figure 35. Type of Stromatolith Structure.

Chief among these remains are the so-called "stromatoliths" (Ref. 5), peculiar calcareous formations constructed in the form of relatively regular cupolas consisting ostensibly of a series of nested cones (Figure 35). They reach a height of up to one meter and a base diameter of up to half a meter. At times they are large bodies with a rounded surface, and are also constructed of separate laminae. In another instance, the stromatoliths are conical, or even acutely conical in shape. This shape is characteristic both for Pre-Cambrian time and for the initial systems of the Palaeozoic. Stromatolith agglomerations formed reefs

and extensive stromatolithic bars characteristic of the shoal waters of the early Sinaean sea (Figure 36).

Extensive laboratory studies of stromatoliths, particularly of polished sections made from them, have demonstrated beyond doubt that these formations are products of the vital activity of ancient photosynthesizing organisms. We have even managed to determine and describe a large number of species, chiefly of blue-green, but also of red algae, which later took part in forming stromatoliths (Figure 37).

Both marine and fresh-water algae were, in general, apparently extensively represented at different periods of the Proterozoic Era, especially in the Sinisian period.

The upper complex of the Riphean, including in particular, the corresponding series of the Urals, the Rüssian platform, and the Sino-Tibetan continental plateau is characterized by powerful development of branching algae (Collenia).

For the lower complexes, we must chiefly mention stromatolith-forming algae, which in some cases are rock-forming. For example, the bottom of the Ural Riphean and of the Sinisian of the Sino-Tibetan continental plateau are characterized by such species as Canophyton cylinducus.

The organically secreted limestone deposits found in the Sahara are classified as the beginning of the stromatoliths (Ref. 6). These algae reefs are apparently the very earliest bioherms\* known in geological history. They are more than a billion years old.

Vologdin indicates, however, that the preponderant number of the oldest alga species did not organize distinct bodies of constant stromatolithic form, but laid down a deposit and converted it into solid rock, where only the morphology of their colonies and the products of their vital activity are partially preserved. The state of studies on these most ancient algae is still very low, but in recent years Vologdin has discovered a great variety of genera and /196 species of blue-green and red algae in layers of marine deposits formed in the Sinisian period (Ref. 7).



Figure 36. View of Stromatolithic Bar Formed by the Alga Crustophicus ongaricus (lower photograph).

This period may be described as the second half of the transitional period /197 between the preactualistic and actualistic eras on the Earth's surface. At this time, the atmosphere was already becoming enriched to a substantial degree with free oxygen, and it may be assumed that the early stromatoliths played an important role in this enrichment. Consequently, they possessed the capacity to photosynthesize. We know, however, that organisms which photosynthesize must be endowed with a very differentiated and very advanced intracellular

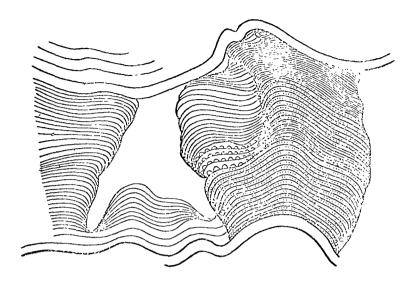


Figure 37. Stromatolith Types Formed by Different Algae

apparatus, which could be formed only as the result of very lengthy evolution of original living beings and only long after the development of life. Therefore, in our search for life we must plunge into far more ancient periods in the existence of our planet. The traces of life preserved from these periods are extremely few in number, however, and are always random in nature. This very seriously prejudices the reliability of conclusions drawn from studying these traces.

A very interesting statement by A. Vologdin is that the green-blue algae in the stromatoliths must often have been attended by iron bacteria, which at times predominated in intervegetative periods and formed ferriferous films in the stromatoliths.

Since iron bacteria chemosynthesize (Ref. 8) and produce energy by oxidizing ferrous into ferric oxide, they absolutely required molecular oxygen; there could have been considerably less molecular oxygen in the atmosphere in this transitional period which we are analyzing than there is now. They could derive it in part from the algae, in symbiosis with which they formed stromatolithic concentrations of iron hydroxides and calcium carbonate. "At times," writes Vologdin (Ref. 9), "bacterial activity alternated with algal activity: summer was the time of optimum algal development, winter that of predominant iron-bacterial development." The result of this was the complexity of certain stromatoliths, where limestone alternates with ferric hydroxide (Figure 38). Vologdin believes that iron bacteria were already in existence at the very beginning of the Proterozoic, and even at the beginning of the Archeozoic era, but this assertation requires far more extensive factual material than is presently at our disposal.

The most ancient true fossils are now considered to be the remains of

organisms preserved in iron ores of Southern Ontario (Canada) and described by Tyler and Barghoorn (Ref. 10). These organic remains were probably converted into fossils under the conditions of their habitat by silicon substitution of the original substance molecule by molecule. In this process, their internal structure was preserved in the finest detail. From a study of this structure, the conclusion was drawn that some of the forms found were primitive algae and others, fungi.

/198



Figure 38. Layers of Algal Deposits Forming a Stromatolith. Polished Section. X 10.

It is understandable that a conclusion of this sort is very rough and preliminary and that of course, absolutely no solution to the problem of the nature of metabolism in these organisms can be based upon it. For example, it cannot be said whether those forms, which are classed as "algae", were actually capable of photosynthesis. It is also very difficult to determine the absolute age of these fossils. On the basis of findings of the rubidium-strontium method, this age is tentatively set at 1600 million years. Consequently, the organisms whose remains were preserved in Ontario lived in the transitional era and may have been either anaerobes or aerobes.

The comparative biochemical findings which we presented above absolutely indicate however, that the germination of life and its initial stages of development proceeded under reducing-atmosphere conditions in the preactualistic era. Geologists date the end of this era at two billion years ago, and thus the development of life must be moved back to even more remote times.

The most ancient manifestations of life are now believed to be the lime secretions discovered by A. McGregor (Ref. 11) in the dolomitic series in Southern Rhodesia (South Africa). Here there are no true fossils with structurally preserved remains of previous organisms, but the limestone quite distinctly reveals a laminar structure of apparently nested cones which is hard to regard /199 as the result of abiogenic processes. To a certain degree, these formations structurally resemble the deposits resulting from the vital activity of limesecreting algae (stromatoliths), which, however, lived in a much later geological epoch. Because of this resemblance, the Rhodesian deposits are often called algal limestones, but this is incorrect, of course, since no conclusion can be drawn as to definite relationships between the organisms which formed these deposits merely from the structural similarity of secreted deposits.

Based on an isotope analysis of the granitic veins cutting through the limestone secretions in Rhodesia, the age of the latter is assumed to be about 2700 million years. Hence, they indubitably belong to the preactualistic era. The attempt, based merely on the form of the deposits, to attribute to the organisms which formed them the same metabolism as that of later aerobic algae

is completely groundless — particularly because lime can easily be secreted in anaerobic metabolism. At the same time, there is some reason to assume that the producers of the Rhodesian limestone secretions had no definite morphological structure, but represented a mass of irregular shape. Perhaps they were not even primitive organisms, but our hypothetical protrobions — if so, we have closely approached the time at which life originally developed.

A study of even more ancient rocks no longer reveals any direct signs of life, and we can draw our own conclusions about these remote periods in the Earth's history only from study of geochemical materials (Ref. 12), but the results obtained from this may frequently be interpreted in different ways. For example, very valuable data may thus be derived from an isotopic analysis of deposits of graphite or Pre-Cambrian coals. For the most ancient of them, however, we still cannot say whether these deposits were formed from the organic substances of the "primary broth", from coacervate droplets, from protobions, or even from already-formed living beings, i.e., whether they formed before or after the development of life. For purposes of clarity, we shall give a table (Table 7) which we have borrowed from A. Vologdin's book Zemlya i zhizn' (Earth and Life), since this table gives a very clear view of the change in eras and geologopalaeontological systems in the evolutional history of the Earth.

It is our opinion, however, that we still do not have in hand the factual material which would permit us more or less accurately to determine the time that life began (as the author of this table does). However, it may be confidently stated that between the development of the "primary broth" and the formation of the most primitive organisms, which can be detected in the form of fossils, there lie vast stretches of time, a long road of gradual perfection of metabolism, of molecular and supramolecular structures.

It is characteristic of the evolutional development of matter that it proceeds at a continuously accelerating tempo, as though on a steep upward curve. Abiogenic evolution of organic substances required billions of years. With the rise of life, the development went on much faster. Essential shifts on the evolutionary path of life occurred in the course of hundreds and tens of millions of years. The formation and biological development of man has taken only a million years. Social transformations have been accomplished in the course of millen- /203 nia and centuries. And now we easily note major events in the development of human society in periods calculated in decades.

We must always bear this development pattern in mind, both when we analyze the events of the remote past and in our forecasts of the future.

When any new form of the motion of matter arises, the old forms are retained, but their role in further progress is negligibly small since their rates of development are several orders lower than developmental rates of the new form of motion. We saw this in the example of the rise of life when old abiogenic methods of synthesis of organic substances dropped into the background, as compared to the faster biological syntheses. This also holds true in the transition from the biological form of motion to the social.

It is doubtful that in the last thousand years man has appreciably changed

154

TABLE 7. HISTORY OF THE EARTH'S CRUST AND OF LIFE

			_
System	Principal Groups of Organisms	Absolute Age (Millions of Years Ago)	
Anthropo- genic	Man, mammals and many groups of marine and fresh-water mollusks, corals, sea urchins and lilies, sponges, foraminifera	1-0	/200
Neogenic	Various mammals, including Hipparia (ances- tors of the horse), anthropoid apes	1-25	
Paleogenic	Mammals (lowest apes appear), Reptilia; among invertebrates Pelecypoda, gastro- pods, nummulites, Orbitoides; among algae Bacillarieae	70-25	
Cretaceous	teleosts; birds; among invertebrates	140 <b>-</b> 70	
Jurassic	Massive development of Reptilia and Amphibia (dipnoans), mammals (few), teleosts (few), reef-forming corals, ammonites; oysters; among insects Lepidoptera	185-140	
Triassic	Appearance of first mammals and teleosts; many Reptilia terrestrial, aquatic, fly- ing; among invertebrates marine lilies, ceratites, ammonites, belemnites, Beller- ophontidae	225 <b>–1</b> 85	
Permian	Amphibia, primitive Reptilia; among inverte- brates brachiopods, Goniatites, ammon- ites, Pelecypoda, bryozoans; among land plants ferns, gymnosperms in the form of the first evergreens, gingkos, corda- ites	270-225	
Carboni- ferous	Among vertebrates shark-like fish; among invertebrates Goniatites, Nautiloidiea; among plants seed ferns and cordaites, spore-bearing plants, lycopods, lepidophytes, calamites, Sphenophyllales. Many amphibians stegocephalians etc. First reptiles	. 320–270	
	Anthropo- genic  Neogenic  Paleogenic  Cretaceous  Jurassic  Triassic  Permian	Anthropogenic  Man, mammals and many groups of marine and fresh-water mollusks, corals, sea urchins and lilies, sponges, foraminifera  Neogenic  Various mammals, including Hipparia (ancestors of the horse), anthropoid apes  Paleogenic  Mammals (lowest apes appear), Reptilia; among invertebrates Pelecypoda, gastropods, nummulites, Orbitoides; among algae Bacillarieae  Cretaceous  Mammals, massive development of Reptilia and teleosts; birds; among invertebrates oysters, belemnites, calcareous Globigerinidae, Rotalia, and Orbitolina  Jurassic  Massive development of Reptilia and Amphibia (dipnoans), mammals (few), teleosts (few), reef-forming corals, ammonites; oysters; among insects Lepidoptera  Appearance of first mammals and teleosts; many Reptilia terrestrial, aquatic, flying; among invertebrates marine lilies, ceratites, ammonites, belemnites, Bellerophontidae  Permian  Amphibia, primitive Reptilia; among invertebrates brachiopods, Coniatites, ammonites, Pelecypoda, bryozoans; among land plants ferns, gymnosperms in the form of the first evergreens, gingkos, cordates  Carboni-  ferous  Among vertebrates shark-like fish; among invertebrates Goniatites, Nautiloidiea; among plants seed ferns and cordaites, spore-bearing plants, lycopods, lepidophytes, calamites, Sphenophyllales. Many amphibians stegocephalians etc. First	Anthropogenic from a mamals and many groups of marine and fresh-water mollusks, corals, sea urchins and lilies, sponges, foraminifera 1-0  Neogenic Various mammals, including Hipparia (ancestors of the horse), anthropoid apes 1-25  Paleogenic Mammals (lowest apes appear), Reptilia; among invertebrates Pelecypoda, gastropods, nummulites, Orbitoides; among algae Bacillarieae 70-25  Cretaceous Mammals, massive development of Reptilia and teleosts; birds; among invertebrates oysters, belemnites, calcareous Globigerinidae, Rotalia, and Orbitolina 140-70  Jurassic Massive development of Reptilia and Amphibia (dipnoans), mammals (few), teleosts (few), reef-forming corals, ammonites; oysters; among insects Lepidoptera 185-140  Triassic Appearance of first mammals and teleosts; many Reptilia terrestrial, aquatic, flying; among invertebrates marine lilies, ceratites, ammonites, belemnites, Bellerophontidae 225-185  Permian Amphibia, primitive Reptilia; among invertebrates brachiopods, Goniatites, ammonites, Pelecypoda, bryozoans; among land plants ferns, gymnosperms in the form of the first evergreens, gingkos, cordaites  Carboni- ferous Among vertebrates shark-like fish; among invertebrates shark-like fish

TABLE 7 of	continue	Ċ
------------	----------	---

		TABLE 7 continued	3
Era	System	Principal Groups of Organisms	Absolute Age (Millions of Years Ago)
Palaeo- zoic	Devonian	First terrestrial amphibians appear. Crossopterygii and Dipnoi, Loricata. Among invertebrates tetraradiate corals flourish; calceolate, spiriferids, pentamerids, Goniatites, trilobites, sea lilies; among plants Psilophitales, disappearing by the end of the period, development of lycopods, arthrophytes, beginning of gymnosperms. First terrestrial plants	<u>/201</u> 400-320
	Silurian	Vertebrates cartilaginous fishes, primitive fish-like Agnatha. Among invertebrates numerous brachiopod mollusks, arthropods (crustaceans, trilobites), graptolites, tetraradiate corals; sea lilies appear. Among plants considerable development of algae blue-green and red	420-400
	Ordovician	Loricata; among crustaceans ostracods, Phyllopods, trilobites; graptolites, tetra- radiate and tubular corals; brachiopods; early representatives of bryozoans; Nautil- oidea. Massive development of algae	
D .	Cambrian	First Loricata, trilobites, and crustaceans.  Appearance of graptolites, sponges, Stromatoporoidea, brachiopods, primitive Nautiloidea. In Lower and Middle Cambrian — massive development of Archaeocyatha.  Abundance of red and blue-green algae	570-480
Proter-	Sinisian	Massive development of unicellular and multi- cellular blue-green (more rarely, red and green) algae; at the end of the period, early Archaeocyatha, sponges, worms, and medusas appear	1200–570
	Yenisei	Massive development of unicellular blue-green algae; development of iron and other bacteria	1500-1200
	Sayan	Development of unicellular algae and iron and other bacteria	1900-1500
1			

<u>-</u>		TABLE 7 continued	
Era	System	Principal Groups of Organisms	Absolute Age (Millions of Years Ago)
Archeo- zoic	Not divi- ded into systems	Appearance of virus-like organisms, bacteria, oxidizing mineral substances, soil bacteria; development of algae. Chemical transformation of primoridal carbon compounds. Predominance of chemical reactions in transformation of mineral substance of terrestrial crust.	
Catarch- eic	-Not divi- ded into systems	Chemical processes in the Earth's crust, massive appearance of volcanism and magnetism, start of formation of water basins on Earth's surface by condensation of water vapor of the "secondary" atmosphere. Generation of insignificant amounts of oxygen in action of cosmic rays on water vapor in atmosphere. General reductive nature of prebiosphere.	3500-2700
	tion o	gical stage of Earth's development forma- f the planet by concentration of cosmic mate- Primary atmosphere "stripped away".	More than 3500

Note. The Sayan\* and Yenisei\* systems are classified by the author according to Siberian data based on discovery of algae in their strata. The Sinisian system was isolated in China where it has been well studied.

biologically, but in that time he has acquired a previously unparalleled power over nature surrounding him. This power of his is the result of public, social, not individual biological development.

The broad highway of human progress is even now passing not through the biological development of individual human personality, but through the advancement of his entire social life, through progress in the social form of the motion of matter.

### REFERENCES

- 1. Keller, B. Priroda, No. 9, p. 30, 1959.
- 2. Vologdin, A. Paleontologiya i poiski poleznykh iskopayemykh (Palaeontology and the Search for Useful Minerals). Izdatel'stvo "Znaniye", 1960.
- 3. Naumova, S. Paleontologiya, No. 4, 1963.
- 4. Vologdin, A. Izvestiya Akademii Nauk SSSR, Seriya geologicheskaya, No. 2,

<sup>\*</sup>Translator's Note: This pertains to Sayan Mountains and Yenisei River in the USSR.

- 5. Vologdin, A. Priroda, No. 9, 1955.
- 6. Gravelle, M., Lelubre, M. Bull. Soc. Geol. Fr. 7, 435, 1957.
- 7. Vologdin, A. Drevneyshiye vodorosli SSSR (The Most Ancient Algae in the USSR). Izdatel'stvo Akademii Nauk SSSR, 1962.
- 8. Kholodnyy, N. Zhelezobakterii (Iron Bacteria). Izdatel'stvo Akademii Nauk SSSR, 1953.
- 9. Vologdin, A. Zemlya i zhizn' (Earth and Life). Izdatel'stvo Akademii Nauk SSSR, 1963.
- 10. Tyler, S., Barghoorn, E. Science, 119, 606, 1957.
- 11. McGregor, A. Trans. Geol. Soc. S. Afr., 43, 9, 1940.
- 12. Abelson, P. Trudy V Mezhdunarodnogo biokhimicheskogo kongressa. Simpozium III (Transactions of the Fifth International Biochemical Congress. Symposium III.) Izdatel'stvo Akademii Nauk SSSR, p. 59, 1962.
- 13. Manskaya, S., Drozdova, T. Geokhimiya organicheskogo veshchestva (The Geochemistry of Organic Matter). Izdatel'stvo "Nauka", 1964.

Scientific Translation Service 4849 Tocaloma Lane La Canada, California NASw 1496

158 NASA-Langley, 1968 — 4 F\_488

# NATIONAL AERONAUTICS AND SPACE ADMINISTRATION WASHINGTON, D. C. 20546

OFFICIAL BUSINESS

#### FIRST CLASS MAIL

POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

OT DOT 2) 51 30S 65166 00903 TIM FORCE MEANING LABORATORY/AFAC/ ELECTRIC AIR FORCE BASE, 45% MEYTRO 87117

ALL MISS AADFLINE F. CARDVA, CHIEF TECHNICAL

POSTMASTER: If Undeliverable (Section 158 Postal Manual) Do Not Return

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

-National Aeronautics and Space Act of 1958

# NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

#### TECHNICAL MEMORANDUMS:

Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

# TECHNOLOGY UTILIZATION

PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Notes, and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546